VOL. XXV. [DECEMBER, 1903.] NO. 12.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 77.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[THIRD PAPER.]

BY ALLEN ROGERS AND EDGAR F. SMITH.

Received September 25, 1903.

BY REFERENCE to the American Chemical Journal, 7, 413, there will be found a classification of the various groups of "complex inorganic acid" derivatives obtained by Wolcott Gibbs—the pioneer in this field of research. There will not be observed in that grouping any derivatives in which there are four different acid radicals acting as a compound anion. It has been the purpose of the present investigation to ascertain whether dioxides could be introduced into complexes consisting of sesquioxides, pentoxides and trioxides. It was hoped that by boiling ammonium vanadico-phospho-tungstate with an excess of silicic hydrate such a result would be reached, but combination did not ensue. The various constituents were then separately brought together and boiled with an excess of ammonium hydroxide for a period of six hours. Some dioxide did enter the combination, but it was concluded to operate in neutral solution; accordingly, 30 grams of ammonium paratungstate, in 700 cc. of water, were boiled ten hours in the presence of an excess of the hydrate of the particular dioxide which it was desired to introduce, after which 2 grams of ammonium phosphate were added, the solution being then boiled

two hours longer, when 8 grams of ammonium metavanadate, reduced to the hydrate of the trioxide,[1] were added and the whole boiled for two hours more. This was the general method of preparation; hence, it will not be repeated in connection with the several derivatives which are described later.

In studying the behavior of these products, no tests were discovered which would differentiate one body from another. The following observations apply equally well to all. The salt separated from a concentrated aqueous solution in large, brilliant, black, octahedral crystals. These were very soluble in water, but were insoluble in organic reagents. Nitric acid, added to the solid salts, served to decompose them, a yellow-colored body resembling tungsten trioxide separating, but disappearing completely on the addition of water, and yielding a yellow-colored solution.

Dilute or concentrated nitric acid, added to the solution of the salts, merely caused a change in its color, without producing a precipitate. Hydrochloric acid caused a color change in the solution very slowly only on boiling.

Ammonium hydroxide did not alter the salt solutions. Sodium hydroxide produced a gray precipitate, which dissolved, on boiling, with the evolution of ammonia. A dark brown precipitate was produced by silver nitrate. It dissolved, to some extent, in boiling water. Ammoniacal silver nitrate produced an olive-green colored precipitate. It dissolved completely when the solution was boiled.

The precipitate, light green in color, formed by mercurous nitrate, was insoluble in water, but readily dissolved upon the addition of a few drops of nitric acid. The lead precipitate acted similarly. Mercuric chloride caused no precipitation. The same was true of copper sulphate, while a solution of ammoniacal copper sulphate produced a dirty gray precipitate, insoluble in boiling water. Cadmium chloride gave no reaction. Ammoniacal cadmium chloride threw out a dirty gray precipitate, insoluble in boiling water, but dissolved by water containing a few drops of hydrochloric acid. Cobalt nitrate, in ammoniacal solution, produced a bottle-green colored precipitate, which, changed to an

[1] The hydrate of the trioxide is produced when ammonium meta-vanadate is boiled for half an hour with hydrochloric acid, then evaporating to dryness upon a water-bath. The residue, taken up in water, imparts to the latter a copper-green color. Ammonium hydroxide was added to the solution. The resulting precipitate (hydrate of vanadium trioxide), after being washed once or twice with dilute ammonium hydroxide, was introduced into the tungstate solution.

olive-green on boiling. Barium chloride, in neutral solution, was without any action, but in the presence of ammonia and upon boiling, threw down a heavy insoluble precipitate. In the analysis of the salts mentioned below, the method described in previous communications proved inadequate. The difficulties met in this portion of the investigation were great. They were, in the main, surmounted. After much search, with frequent failures, the following course was adopted and gave, it is believed, reliable results.

In each case the air-dried salt was gently and gradually heated to dull redness. The loss represented water and ammonium oxide. The residue was then fused with equal parts of sodium carbonate and potassium nitrate. The fusion was taken up with water containing ammonium hydroxide and ammonium nitrate, boiled for several minutes and then filtered. The insoluble portion was thoroughly washed, dried, ignited and weighed as MeO_2. A "magnesia mixture" was added to the cold filtrate and washings. The magnesium ammonium phosphate was dissolved and reprecipitated. The tungstic acid, in the filtrate from the phosphoric acid precipitate, was determined according to the method of Gibbs, modified by Friedheim.[1] The vanadium was obtained by difference. The ammonium oxide was estimated in the usual manner.

A few words regarding the nomenclature, used in this communication, may not be out of place. An inspection of the literature relating to "complex inorganic acids" will disclose confusion on this point. After reflection, it was concluded to terminate the names of the dioxides, MeO_2 in *oso;* those of the type of Me_2O_3 in *ico,* and those of the form of Me_2O_5 in *o* or *io*. It is admitted that this system is not satisfactory and is contradictory to our generally accepted ideas on the subject, yet it seems to be the only means of indicating a differentiation in the types of oxides in these complexes.

AMMONIUM SILICOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(NH_4)_2O$	5.42	5.37	5.40
SiO_2	0.56	0.67	0.68
V_2O_3	15.83	15.77	15.80
P_2O_5	1.33	1.35	1.34
WO_3	60.32	60.58	60.45
H_2O	16.41	16.26	16.32

[1] *Ber. d. chem. Ges.* (1890), p. 353.

AMMONIUM TITANOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.	Per cent.
$(NH_4)_2O$	5.48	5.55	5.48	5.45
TiO_2	0.66	0.65	0.72	0.50
V_2O_5	18.98	19.10	18.89	18.87
P_2O_5	2.45	2.44	2.75	2.52
WO_3	56.29	56.08	56.50	56.42
H_2O	16.14	16.18	16.01	16.24

AMMONIUM ZIRCONOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(NH_4)O_2$	5.35	5.43	5.39
ZrO_2	0.63	0.59	0.61
V_2O_5	14.28	14.22	14.25
P_2O_5	2.49	2.55	2.52
WO_3	62.29	62.18	62.24
H_2O	14.96	15.03	14.99

AMMONIUM THOROSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(NH_4)_2O$	5.42	5.40	5.41
ThO_2	0.77	0.80	0.79
V_2O_5	16.03	16.31	16.17
P_2O_5	2.52	2.71	2.61
WO_3	59.31	58.94	59.13
H_2O	15.95	15.84	15.89

AMMONIUM STANNOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.	Per cent.
$(NH_4)_2O$	5.34	5.40	5.38	5.37
SnO_2	0.25	0.23	...	0.24
V_2O_5	12.33	12.47	...	12.40
P_2O_5	2.34	2.38	2.36	2.36
WO_3	65.51	65.29	65.20	65.40
H_2O	14.23	14.23	....	14.23

The reactions of ammonium vanadico-phospho-tungstate are vastly different from those obtained after the introduction of a dioxide into its composition, even if the quantity of that dioxide be small. In mineral analysis the influence of such minute amounts of supposedly adventitious constituents is too often disregarded and not considered in the deduction of formulas.

The reader will grant that there is in the above analytical results satisfactory concordance. The dioxide was extremely difficult to eliminate entirely from the remaining components of the anion, so that while it is thought the percentages given are correct, yet, if there be an error in this factor, when corrected, it will prove to be above rather than below the amount here given.

The formulas deduced from the preceding figures of analysis are imposing and appear rather improbable, so that, for the present, they can be omitted, as the introduction of other dioxides is projected. Efforts, too, are being made to find other means of arriving at the molecular magnitudes of these bodies.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 78.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[FOURTH PAPER.]

BY ALLEN ROGERS AND EDGAR F. SMITH.

Received September 25, 1903.

IT may be observed that in those bodies containing vanadium but two oxides of the latter element appear—the trioxide and pentoxide. No derivatives of vanadicotungstic acid ($H_2O.V_2O_3WO_3$) have yet been prepared. In the classification of Wolcott Gibbs they are lacking. Further, the question had arisen whether by reduction of vanadic acid with hydrochloric acid the resulting oxide was really not the same as that produced on reducing vanadic acid with sulphur dioxide. If the stages of reduction were identical, then the hydroxides corresponding to these oxides—V_2O_5 and V_2O_4—if combined with tungstic acid, would yield one and the same complex acid. As will be seen, the products were dissimilar.

AMMONIUM VANADICO-TUNGSTATE,

$$3(NH_4)_2O.V_2O_3.8WO_3.10H_2O.$$

Thirty grams of ammonium paratungstate were boiled for six hours, when 6 grams of vanadium trioxide were introduced and the boiling continued for two hours longer. The filtered solution was reduced to a small volume and allowed to crystallize. Frequently, ammonium tungstate separated first and mixed with the vanadico-tungstate derivative. The crystals were treated several times with ice-water, which did not dissolve the ammonium tungstate, and, on evaporating the solution, ammonium vanadico-tungstate crystallized out in thin crusts, very soluble in water, but insoluble in organic solvents. The addition of nitric acid

to the salt solution changed the color from black to yellow, and tungsten trioxide separated. Hydrochloric acid caused a slight deposition of trioxide. Mercurous nitrate produced an olive-green colored precipitate, insoluble in boiling water, but dissolving upon the addition of a few drops of nitric acid. The silver salt was olive-green in color and only partially soluble in boiling water. Mercuric chloride and copper sulphate produced no precipitates in the neutral aqueous solution of the salt. Ammoniacal cadmium chloride and ammoniacal cobalt nitrate produced precipitates which were insoluble in water. They dissolved on the addition of a few drops of nitric or hydrochloric acid, with the deposition of tungsten trioxide. The barium salt was insoluble in boiling water.

In analyzing the salt, the Gibbs method, modified by Friedheim,[1] was adopted.

		Found.		
	Theory.	I. Per cent.	II. Per cent.	III. Per cent.
$(NH_4)_2O$	6.66	6.56	6.56	6.52
V_2O_3	6.40	6.44	6.39	5.91
WO_3	79.24	79.24	79.26	79.76
H_2O	7.70	7.79	7.79	7.81

AMMONIUM VANADOSO-TUNGSTATE,

$$5(NH_4)_2O.2V_2O_4.14WO_3.13H_2O.$$

Ammonium vanadate, in the presence of sulphuric acid, was reduced with sulphur dioxide and the solution precipitated with ammonium hydroxide. The resulting body, after washing, was added to a boiling solution of ammonium paratungstate. After filtering and evaporating to a small volume, black, well-defined, octahedral crystals separated. These proved to be very soluble in water. Nitric acid changed the color of the black solution to yellow *without*, however, *the separation of tungsten trioxide.* Hydrochloric acid does not change the color of the solution in the cold and only very slowly on boiling. No deposition of trioxide occurred. The mercurous salt was insoluble in pure water, but dissolved on the addition of a little nitric acid. The lead salt behaved in the same way. Mercuric chloride, cadmium chloride and copper sulphate were without action. The last two salts, in ammoniacal solution, did precipitate insoluble compounds, that

[1] *Ber. d. chem. Ges.*, **23**, 353 (1890).

acids dissolved. Ammoniacal cobalt nitrate behaved in the same way. The barium salt, emerald-green in color and insoluble in water, dissolved on the addition of a few drops of acid.

Analysis:

		Found.		
	Theory.	I. Per cent.	II. Per cent.	III. Per cent.
$(NH_4)_2O$	6.38	6.47	6.29	6.33
V_2O_4	8.15	8.30	8.28	...
WO_3	79.72	79.27	79.56	80.43
H_2O	5.75	5.96	5.87	...

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 79.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[FIFTH PAPER.]

BY CLARENCE W. BALKE AND EDGAR F. SMITH.

Received September 25, 1903.

FIFTY years ago Struve made double molybdates, which he believed were analogous to the alums. Wolcott Gibbs showed that the products of Struve's efforts were salts of "complex inorganic acids," in which the various sesquioxides, together with molybdenum trioxide, constituted the several anions in union with protoxides—cathions. It was Struve's intention to prepare analogous tungstates. He never described any of these and, in order to complete certain gaps in a line of inquiry, upon which we have been engaged, we undertook the preparation of compounds following the general types

$$R_2O.\ x\ Al_2O_3\ \ y\ WO_3.$$
$$R_2O.\ x\ Fe_2O_3\ \ y\ WO_3.$$
$$R_2O.\ x\ Cr_2O_3\ \ y\ WO_3.$$
$$R_2O.\ x\ Ni_2O_3.\ \ y\ WO_3.$$
$$R_2O.\ x\ Mn_2O_3.\ y\ WO_3.$$
$$R_2O.\ x\ Bi_2O_3\ \ y\ WO_3, \text{ etc.}$$

All of these have been made. In this communication, however, we shall only describe those derivatives in which aluminum and bismuth oxide are present. The remaining bodies will be

further studied and efforts will be made to introduce certain other sesquioxides. We have also made a number of bodies of these types:

$$R_2O.\ x\ Fe_2O_3.\ y\ P_2O_5.\ z\ WO_3.$$

$$R_2O.\ x\ Ni_2O_3.\ y\ P_2O_5.\ z\ WO_3, \text{ etc., etc.}$$

It may be mentioned that the introduction of the pentoxide apparently increased the stability of the resulting body and caused it to crystallize in a more definite and pronounced form.

AMMONIUM ALUMINICO-TUNGSTATE,

$$3(NH_4)_2O.Al_2O_3.9WO_3.4H_2O.$$

This salt was made by boiling freshly precipitated and thoroughly washed aluminum hydroxide, in excess, with ammonium paratungstate for from fifteen to twenty hours, when the solution was allowed to drain through a folded filter. On evaporating the clear liquid upon a water-bath, a dense, highly refracting sirup appeared. Glass floated on it. On exposure to the air, it dried to a semitransparent mass. It seemed to be a very stable body. Ammonium hydroxide added to its solution did not produce a precipitate. Its dilute solutions were not affected in the hot or cold by dilute hydrochloric or nitric acids.

The dry, powdered salt dissolved in concentrated nitric acid; precipitation did not occur, even upon boiling. The salt was soluble also in concentrated hydrochloric acid without the production, in the cold, of a precipitate, but when the solution was vigorously boiled a yellow-colored precipitate separated. Mercurous nitrate produced, in its aqueous solution, a yellowish white-colored precipitate. The precipitate caused by barium chloride was almost insoluble in hot water. After drying, acids failed to dissolve it. In a slightly ammoniacal solution of the salt, silver nitrate produced a yellowish white precipitate, which proved to be soluble in a large volume of hot water.

ANALYSIS.

The powdered, air-dried salt was further dried by exposure, for several hours, to the temperature of a water-bath. A weighed portion was then ignited at a low red heat in a tared porcelain crucible. The loss it sustained represented water and ammonium oxide. The ignited material was next fused with potassium bisulphate. The fused mass was digested with 125 cc. of water,

15 cc. of nitric acid, and several drops of hydrochloric acid. When the decomposition was complete, the solution was filtered and the aluminum precipitated, with ammonium hydroxide, from the clear liquid. Whenever the resulting aluminum oxide was contaminated with tungstic oxide the fusion was repeated. The ammonium oxide was determined in the usual manner.

Results:

	Theory.		Found.		
	Per cent.	Per cent.	I. Per cent.	II. Per cent.	III. Per cent.
$3(NH_4)_2O$	156	6.45	6.61	6.45	6.42
Al_2O_3	102	4.22	4.12	4.17	...
$9WO_3$	2088	86.35	86.30	86.24	...
$4H_2O$	72	2.98	2.97	3.14	...

SILVER AMMONIUM ALUMINICO-TUNGSTATE,

$$11Ag_2O.21(NH_4)_2O.4Al_2O_3.36WO_3.$$

A yellowish white precipitate was produced when silver nitrate was added to a distinctly ammoniacal solution of the preceding salt. This precipitate was washed with cold water, in which it proved to be but sparingly soluble. Or, it was dissolved in a large volume of hot water, made ammoniacal. The filtrate was allowed to stand, when a crystalline mass separated from it on cooling. Analyses of the precipitated salt and the crystalline body showed them to be identical in composition. Air-dried samples were used for the analysis. The perfectly dry salt was quite insoluble in pure water, but readily soluble in water containing ammonia or nitric acid. Mercurous nitrate, introduced into the nitric acid solution, produced a yellowish white precipitate, readily soluble in hot water.

Analysis.—The silver was determined as chloride in the nitric acid solution of the salt, while the other constituents were estimated as described under the ammonium salt. The loss upon ignition was found to equal the ammonium oxide determined directly.

	Theory.		Precipitated salt. I.	Crystallized salt. II.
	Per cent.	Per cent.	Per cent.	Per cent.
$11Ag_2O$	2552	20.57	20.71	20.48
$21(NH_4)_2O$	1092	8.80	8.87	8.90
$4Al_2O_3$	408	3.29	3.25	3.28
$36WO_3$	8352	67.32	67.17	67.34

If the sum of the protoxides be taken, the formula would read

$$32R_2O.4Al_2O_3.36WO_3,$$

which would furnish the simple formula

$$8R_2O.Al_2O_3.9WO_3,$$

when divided by four.

It may be observed here that Klein[1] has represented the most stable series of borico-tungstates by the general formula

$$2R_2O.B_2O_3.9WO_3.xH_2O.$$

AMMONIUM BISMUTHICO-TUNGSTATE,

$$3(NH_4)_2O.2Bi_2O_3.11WO_3.10H_2O.$$

On boiling well-washed bismuth metahydroxide with ammonium paratungstate for two days, it dissolved in large amount, so that it was necessary to make additions of it from time to time. The solution, filtered from the excess, had a yellow color. It was evaporated to complete dryness and the residue then exhausted with a small quantity of hot water, the solution filtered and allowed to cool, when ammonium bismuthico-tungstate separated as an oil, having a specific gravity slightly above 3.6. This oil, after being washed carefully several times with cold water, dried to a transparent, yellow-colored glass. No precipitate was produced on strongly diluting the solution of this salt with water. Ammonium hydroxide caused no change in its cold dilute solutions, but when the latter were boiled in the presence of ammonia, a copious white precipitate separated. Nitric acid caused no change in the boiling dilute solutions of the salt, but in concentrated solutions precipitation occurred on the addition of concentrated nitric acid. The addition of a large volume of hot water again effected solution. Hydrochloric acid occasioned no change in cold or hot dilute solutions, while tungstic acid separated on boiling with concentrated hydrochloric acid. Mercurous nitrate precipitated yellowish white mercurous bismuthico-tungstate. The results of the analysis were:

	Theory.		Found.		
	Per cent.	Per cent.	I. Per cent.	II. Per cent.	III. Per cent.
$3(NH_4)_2O$ ..	156	4.09	4.34	4.28	4.14
$2Bi_2O_3$.....	930	24.36	24.31	24.22	25.00
$11WO_3$	2552	66.83	66.59	67.07	66.31
$10H_2O$.....	180	4.72	4.76	4.43	4.50

[1] *Ann. chim. phys.* (5), **28**, 350.

POTASSIUM BISMUTHICO-TUNGSTATE,

$3K_2O.2Bi_2O_3.11WO_3.15H_2O$.

This salt separated in the form of a yellow-colored oil, upon adding a hot saturated solution of potassium bromide to a concentrated solution of ammonium bismuthico-tungstate. On cooling, the oil sometimes showed crystals which were very soft and gummy in appearance. It was discovered to be best, when the oil had become viscous and gum-like, to warm it again with a saturated solution of potassium bromide, after which it was repeatedly washed with small volumes of warm water. It was then dried on the water-bath to a transparent, pale lemon-yellow colored glass.

Analysis.—Except for the determination of the potassium the method pursued in the preceding analyses was adopted. In estimating the potassium, a weighed amount of the "glass" was covered with water and mercurous nitrate added in slight excess. Ammonium hydroxide was added to alkaline reaction, the excess of it being expelled by boiling. A few drops more of mercurous nitrate were introduced and, after standing half an hour, the precipitate was filtered off and thoroughly washed with warm water. The filtrate, after acidulation with dilute sulphuric acid, was charged with hydrogen sulphide. The filtrate from the mercury sulphide was evaporated and the potassium obtained as sulphate.

Results:

	Theory.		Found.	
	Per cent.	Per cent.	I. Per cent.	II. Per cent.
$3K_2O$	282	6.99	7.00	7.21
$2Bi_2O_3$	930	23.05	22.72	22.53
$11WO_3$	2552	63.27	63.84	63.88
$15H_2O$	270	6.69	6.44	6.38

STRONTIUM BISMUTHICO-TUNGSTATE,

$3SrO.2Bi_2O_3.11WO_3.11H_2O$.

This salt was made by transposing the potassium salt with a saturated solution of strontium chloride. The product was an insoluble yellow-colored oil, which was washed with hot water to remove all soluble impurities. When cooled, the oil changed to a yellow wax. It was insoluble in pure water, but dissolved readily upon the addition of a few drops of nitric acid. Dried

upon a water-bath, it changed to a hard, vitreous mass. The determination of the strontium was made as described under the potassium salt.

Results:

	Theory.		Found.	
	Per cent.	Per cent.	I. Per cent.	II. Per cent.
$3SrO$	311	7.79	6.80	....
$2Bi_2O_3$	930	23.30	23.07	23.42
$11WO_3$	2552	63.95	....	....
$11H_2O$	198	4.96	4.96	4.95

The purpose of this study will be to ascertain to what extent the more metallic sesquioxides can be introduced into such complexes as have been indicated in the preceding paragraphs, and to exhaustively investigate their derivatives before advancing to those compounds in which there will appear the additional pentoxide.

Columbo- and tantalo-tungstates of sodium and ammonium have been made and analyzed, but a description of them will be reserved for a later communication.

UNIVERSITY OF PENNSYLVANIA.

THE INFLUENCE OF SOIL MOISTURE UPON THE CHEMICAL COMPOSITION OF CERTAIN PLANT PARTS.

BY JOHN A. WIDTSOE.

Received October 7, 1903.

THE great variation in the chemical composition of plants grown under the same climatic conditions and upon similar soils, has always been a somewhat mystifying phenomenon to students of plant chemistry. That plant composition is influenced by soil composition is beyond question; and it is quite generally believed that sunshine, temperature and soil moisture are factors in controlling the chemical composition of plants. However, the relative and absolute values of these soil, climatic and water factors have not been determined, even approximately; and the observed variation in plant composition has usually been beyond satisfactory explanation. In view of this lack of knowledge, it was

most interesting to find a definite relation between the soil moisture and the chemical composition of plants.

In a series of exhaustive experiments on irrigation, carried on by the Utah Experiment Station, the water applied to plants was definitely controlled, and the quantity so varied as to determine the most economical use of water in an irrigated district. All the plants grown in the experiments were subjected to chemical analysis. The full report of the work, in the summer of 1901, is published in Bulletin No. 80 of the Utah Station, and it is upon some of the results there found that the present paper is based.

SOIL CONDITIONS OF THE EXPERIMENTS.

The farm upon which these experiments were conducted is located on the old fossil delta of the Logan River, in Cache Valley, State of Utah. The soil is very shallow—varying in depth from 9 to 59 inches, with an average depth of 28 inches. Below this thin layer of soil is a porous bed, nearly 300 feet deep, composed of coarse gravel, with occasional streaks of sand. It is most probable that this condition of shallow soil, with very porous subsoil, was a strong factor in producing the observed variation in the chemical composition of the crops grown upon the farm. The soil layer is, in most respects, similar to the soils that prevail within the Great Basin Region, as shown by the following physical and chemical analyses. The methods of analysis followed were those prescribed by the Association of Official Agricultural Chemists.

TABLE I.—PHYSICAL COMPOSITION OF THE SOIL.

Depth.	First foot.	Second foot.	Third foot.
Medium sand (0.1 to 0.5 mm.)	28.1	29.7	31.6
Fine sand (0.032 to 0.1 mm.)	25.6	26.4	29.6
Coarse silt (0.01 to 0.032 mm.)	19.2	16.4	14.6
Medium silt (0.0032 to 0.01 mm.)	10.2	6.6	6.6
Fine silt (0.001 to 0.0032 mm.)	2.6	5.6	6.5
Clay (below 0.001 mm.)	8.4	8.8	8.6
Moisture	4.7	4.3	1.8
Soluble and lost	1.2	2.2	0.7
Total	100.0	100.0	100.0

Average weight of one cubic foot of dry soil ..... 88.9 lbs.
Average absolute water capacity ..... 28.56 per cent.

TABLE II.—CHEMICAL COMPOSITION OF THE SOIL.
(All per cents. are referred to the water-free soil.)

	First foot.	Second foot.	Third foot.
Insoluble matter	68.42	65.66	56.49
Potash, K_2O	0.65	0.57	0.43
Soda, Na_2O	0.55	0.53	0.60
Lime, CaO	6.07	8.20	14.81
Magnesia, MgO	5.13	4.13	3.32
Alumina, Al_2O_3	3.13	2.36	2.39
Iron oxide, Fe_2O_3	2.33	2.65	1.72
Phosphoric acid, P_2O_5	0.20	0.15	0.24
Sulphuric acid, SO_3	0.10	0.11	0.08
Carbon dioxide, CO_2	10.00	12.74	17.90
Organic matter	3.86	2.99	2.12
Total	100.44	100.09	100.10
Humus	3.72	1.18	1.06
Nitrogen	0.149	0.100	0.072
Water at 100 C	1.85	1.91	1.69

The plats devoted to these experiments were one-twentieth of an acre in area, well ridged around the edges, so that the water applied would cover the ground to an approximately uniform depth. The depth of water applied at one irrigation varied, ordinarily, from 5 to 7.5 inches. All plants in the same experimental set were treated alike, except as to the quantity of water applied. The amount of water applied is expressed in the depth in inches to which the plats would have been covered had it been applied at one time.

MAIZE KERNELS.

The maize used was of unknown name, but had been grown for many years on the Station farm. It was sown on April 30th, and throughout its life exhibited no extraordinary characteristics, save the variation due to the application of varying amounts of water. The ripe maize was harvested on September 11th. The maize kernels were analyzed with the following results:

TABLE III.—PERCENTAGE COMPOSITION OF MAIZE KERNELS.

Irrigation water applied. Inches.	Water in fresh substance.	Water-free substance.				
		Ash.	Protein.	Ether extract.	Crude fiber.	N-free extract.
7.5	14.01	1.62	15.08	6.02	1.89	75.39
10.0	11.00	1.59	13.42	5.39	2.23	77.37
15.0	11.66	1.65	13.48	6.16	1.91	76.86
20.0	13.00	1.56	12.83	6.29	2.19	77.14
37.3	14.36	1.62	12.52	6.26	1.89	77.72

With one exception, the per cent. of water increased regularly with the increase in the amount of water under which the maize was grown. The per cent. of ash is not regularly affected by the quantity of water used. The protein content is strikingly influenced by the amount of water added to the soil. As the water increases, the per cent. of protein decreases—the difference between the protein content of maize which received 7.5 inches of water and that which received 37.3 inches being 2.56 per cent. The percentage of ether extract was also slightly affected by the soil moisture. As the water applied to the soil increases, the ether extract increases, also.

The per cent. of crude fiber does not seem to be regularly influenced by the soil moisture, but the N-free extract tends to increase on the well-watered plats. In general, the protein in the maize kernel decreases with increased applications of water, while the ether extract and N-free extract increase.

OAT KERNELS.

The variety of oats used in this experiment was "American Banner." The seed was placed in the ground on April 20th, and the ripe crop was harvested on July 30th. The composition of the oat kernel is shown in Table IV.

TABLE IV.—PERCENTAGE COMPOSITION OF OAT KERNELS.

Irrigation water applied. Inches.	Water in fresh substance.	Water-free substance.				
		Ash.	Protein.	Ether extract.	Crude fiber.	N-free extract.
6.98	8.00	3.26	20.79	3.91	9.02	63.02
13.20	7.73	4.52	17.29	4.19	10.76	63.25
14.89	8.11	4.97	15.48	4.21	15.40	59.55
30.00	8.40	4.49	15.49	4.59	10.92	64.51
40.00	8.62	4.55	15.80	4.56	10.38	64.71

As in the case of corn, the per cent. of water in the fresh substance is increased by an increased amount of water. The per cent. of ash does not seem to be affected by the soil moisture. As in the case of corn kernels, the relative amounts of protein are strongly affected by varying the amount of water applied to the soil. The larger the quantity of water, the smaller the per cent. of protein. The highest and lowest per cents. are 20.79 and 15.48—a difference of 5.31 per cent.

The per cent. of ether extract is highest in the well-watered plats, and the variation follows quite regularly the amounts of

water used. The difference between the highest and lowest per cent. is 0.68. The highest per cent. of crude fiber is found on the plat receiving an intermediate amount of water. The N-free extract increases with an increase in the amount of water; this variation is regular, with one exception. As in the case of corn, increasing the water applied to oats, decreases the per cent. of protein, and increases the ether extract and N-free extract.

WHEAT KERNELS.

The variety of wheat used was "New Zealand." It was planted on April 13th, and harvested on July 29th and 30th and August 5th. Table V shows the results obtained from the chemical analysis of the wheat kernels from the different plats.

TABLE V.—PERCENTAGE COMPOSITION OF WHEAT KERNELS.

Irrigation water applied. Inches.	Water in fresh substance.	In water-free substance.				
		Ash.	Protein.	Ether extract.	Crude fiber.	N-free extract.
4.63	7.70	2.70	26.72	2.37	5.44	62.77
5.14	8.16	3.32	25.11	5.24	3.05	63.28
8.81	8.25	2.96	21.25	3.63	4.38	67.75
10.30	8.47	2.54	19.93	2.09	4.47	70.97
12.36	8.14	3.12	22.18	2.12	4.31	68.27
17.50	7.59	2.79	18.57	2.34	5.88	70.43
21.11	6.80	2.50	16.99	1.97	3.92	74.62
30.00	8.70	4.50	15.26	1.85	3.19	75.20
40.00	8.01	2.72	18.43	1.94	3.42	73.48

There seems to be no regular variation in the per cent. of water, held by the fresh substance, to correspond with the amounts of water applied to the soil; neither does the per cent. of ash show any definite connection with the soil water. The per cent. of protein increases very markedly in the wheat kernel as the amount of water applied to the soil decreases. The plat that received 30 inches of water yielded wheat containing 15.26 per cent. protein, while the wheat from the plat that received 7.70 inches, contained 26.72 per cent.—a difference of 11.46. It is to be noted that the variation did not follow regularly the amounts of water used.

The variation in the ether extract are very irregular. The kernels raised with 5 to 8 inches of water contain the highest per cents. of fat. The crude fiber is not strongly affected by the soil water, though the tendency is for the per cent. to decrease as the amount of soil water increases. The per cent. of N-free

extract is highest in the wheat from the plats that received most water. As with corn and oats, increased watering of wheat decreases the per cent. of protein, and increases the per cents. of ether extract and N-free extracts.

POTATO TUBERS.

The variety of potatoes known as "Early Rose" was used in this experiment. They were planted on May 1st and 7th, and were dug on October 22d. They were immediately sampled and subjected to chemical analysis. Traces of reducing sugar were found in all the samples, and a trace of sucrose in one sample. The quantitative determinations are exhibited in Table VI.

TABLE VI.—PERCENTAGE COMPOSITION OF POTATOES.

Irrigation water applied. Inches.	Water in fresh substance.	In water-free substance.						
		Ash.	Protein.	Ether extract.	Crude fiber.	Starch.	Undetermined.	N-free extract.
8.08	76.00	6.68	11.83	0.55	2.69	69.95	8.30	78.25
10.00	76.34	4.57	12.57	0.11	2.46	69.55	10.74	80.29
15.00	75.54	4.85	12.52	0.33	2.21	72.58	7.50	80.08
20.00	76.24	4.29	11.46	0.50	2.56	76.25	4.94	81.19
27.00	75.95	4.99	10.77	0.06	1.93	75.10	7.15	82.25
39.99	76.00	4.87	8.33	0.79	2.06	76.48	7.47	83.95

It is quite noteworthy that the variation in the amount of moisture in the fresh potatoes is very small. In fact, the soil moisture seems to have little, if any, effect on the water content of potatoes. The per cent. of ash does not vary with the amount of water applied. As in the case of the grains, the relative amount of protein becomes larger as the irrigation becomes smaller. The one exception to this rule is the plat which received least water. The difference between the maximum and minimum per cents. is 4.24—sufficient to affect, materially, the food value of the potatoes. The variation of the ether extract is very irregular and does not follow the variation in the amount of water applied to the soil. The crude fiber shows a tendency to decrease on the well-watered plats. The per cent. of starch, on the other hand, increases very regularly with the increased irrigation. The difference between the highest and lowest per cents. of starch is 6.93—also quite sufficient to affect the food value of the tubers. The undetermined portion does not vary regularly with the soil moisture, but there appears to be a tendency for it to decrease as the watering becomes more liberal.

SUGAR-BEETS.

The German Kleinwanzlebener seed was used in these investigations. Seeding was done on April 25th and 26th. The beets were harvested on October 22d. The composition of the beets on the date of harvesting is shown in Table VII.

TABLE VII.—PERCENTAGE COMPOSITION OF SUGAR-BEETS.

Irrigation water applied. Inches.	Water in fresh substance.	In water-free substance.								
		Ash.	Protein.	Ether extract.	Crude fiber.	Reducing sugars.	Sucrose.	Starch.	Undetermined.	N-free extract.
12.32	76.23	4.76	9.68	0.29	5.37	1.22	60.85	6.33	11.51	79.91
15.57	75.95	5.14	8.15	0.31	5.24	1.17	63.20	6.33	10.43	81.13
17.64	75.34	4.38	10.51	0.32	4.80	1.24	61.62	6.19	10.96	80.01
20.06	76.46	4.89	10.42	0.36	5.06	0.94	60.83	6.91	10.59	79.27
21.00	78.67	4.98	7.50	0.18	6.02	1.53	57.21	7.46	15.12	81.32
25.31	75.69	4.69	8.98	0.36	4.98	0.64	62.93	7.10	10.13	80.80
40.82	77.58	4.69	5.63	0.45	5.68	1.18	62.01	7.05	13.31	83.55
53.96	73.39	3.79	6.10	0.36	4.79	1.89	60.65	7.07	15.35	84.96

The per cent. of water in the fresh substance does not vary, in general, with the variation in soil moisture. The per cent. of ash is irregular and does not follow the soil moisture. The per cent. of protein tends to increase with increased applications of water, until 20 inches have been applied; from then on there is a distinct decrease. The difference between the highest and lowest per cent. is 2.92. The per cents. of ether extract, crude fiber and reducing sugars are so irregular that they cannot well be connected with the variation in the soil moisture. The sucrose, which is the most important constituent of the sugar-beet, constitutes from 57.21 per cent. to 63.20 per cent. of the water-free substance. Regular changes in the soil moisture do not seem to cause corresponding regular variations in the sucrose content. This is surprising, in view of the comparative regularity with which the nitrogen-free extract in the crops, previously studied, has increased with the increase in soil moisture. The per cent. of starch increases somewhat with the increase in soil moisture.

From these data, it would seem that the relative proportions of the constituents are not markedly affected by variations in soil moisture. The great regularity in variation that has prevailed

in other crops leads to some doubt concerning the correctness of this view. The plats on which the sugar-beets were grown were very different in depth and in the proportion of gravel, and they had been manured differently. Further, the accurate sampling of beets is a matter of great difficulty. It must also be remarked that the beet was dried and ground before analysis, which is not the best method to be followed in making carbohydrate determinations in sugar-beets. While the per cent. of total carbohydrates may be very near the truth, the sucrose and other single constituents may have suffered change during the process of drying. These questions must be left, however, for future investigations.

To obtain fuller and more accurate data on the effect of soil moisture upon the sugar content and purity of the juice, the plats were sampled and the beets analyzed weekly, from August 19th to October 16th. The average results for the sugar in the juice are found in Table VIII.

TABLE VIII.—PER CENT. OF SUCROSE IN THE JUICE FROM SUGAR-BEETS.

Irrigation water applied. Inches.	August 19th to September 3rd.	September 10th to September 25th.	October 2nd to October 16th.
11.16 to 17.78	11.35	13.14	14.83
19.95 to 26.66	12.58	13.72	15.86
40.82 to 53.96	13.40	14.62	15.25

It is quite evident, from the above table, that during the first two periods, the per cent. of sugar in the juice increases with the increase in the amount of water applied. During the last period, the beets grown with more than 40 inches of water contain 0.61 per cent. less sugar than do those grown with an average of 23.31 inches of water. The general conclusion to be drawn from this table is, that increasing the soil moisture tends to increase the per cent. of sugar in the juice of sugar-beets.

TABLE IX.—PER CENT. PURITY IN JUICE FROM SUGAR-BEETS.

Irrigation water applied. Inches.	August 19th to September 3rd.	September 10th to September 25th.	October 2nd to October 16th.
11.16 to 17.78	77.0	77.9	81.1
19.95 to 26.66	80.6	81.1	82.7
40.82 to 53.96	80.5	82.7	84.2

Table IX shows very clearly that the purity of the juice is highest with sugar-beets grown with large amounts of water but that the differences are so small as to have little practical value.

DISCUSSION.

A study of the preceding tables confirms the belief that the soil moisture influences strongly the chemical composition of plants and plant parts. To what extent the compositions of different plants and plant parts are affected by soil moisture, cannot, of course, be determined from this preliminary investigation. However, it may safely be concluded that the protein and nitrogen-free extract are influenced more than any other chemical group contained by plants. It may further be concluded that withholding water from the plant increases the per cent. of protein, and diminishes the per cents. of nitrogen-free extract and fat; increasing the supply of water decreases the per cent. of protein and increases the per cents. of nitrogen-free extract and fat.

That the variation is far greater than that ordinarily assumed to be possible is shown by Table X, in which the differences between the lowest and highest per cents. of protein, fat, nitrogen-free extract and starch are given, due regard having been had for the variation due to the application of different amounts of water.

TABLE X.—DIFFERENCE BETWEEN HIGHEST AND LOWEST PER CENTS. DUE TO VARYING SOIL MOISTURE

Substance.	Protein.	Fat.	N-free extract.	Starch.
Corn kernels	2.56	0.90	2.33	...
Oat kernels	5.31	0.68	1.69	...
Wheat kernels	11.46	1.78	12.43	...
Potatoes	4.24	...	5.70	6.93
Sugar-beets	4.88	...	5.05	...

While the power to control the composition of plants by varying the soil moisture is of immense practical value to all irrigated countries, yet its higher theoretical importance must not be overlooked. To the plant physiologist it opens a large field of research, which promises to result in light being thrown on some of the obscure parts of our knowledge of plant growth and plant life. The temptation to theorize, even with the meager data of this paper, is very great, but as considerable material on this subject has been gathered since 1901, the discussion of the physiological relations of the data, here presented, has been left for future reports. However, it may be said that the soil moisture is only one of many factors controlling the composition of

plants, and that the great variations, recorded in this paper, were partly due to the peculiar soil conditions prevailing on the Station farm.

This investigation has been continued since 1901, and is still being continued.

CHEMICAL LABORATORY, UTAH EXPERIMENT STATION, LOGAN, UTAH.

[CONTRIBUTION FROM THE NEW YORK AGRICULTURAL EXPERIMENT STATION.]

RENNET ENZYME AS A CAUSE OF CHEMICAL CHANGES IN THE PROTEIDS OF MILK AND CHEESE.

BY L. L. VAN SLYKE, H. A. HARDING AND E. B. HART.

Received September 23, 1903.

INTRODUCTION.

THE object of the work described in this article was, primarily, to ascertain to what extent the proteolytic phenomena, observed in cheese-ripening, are due to the action of an enzyme contained in the rennet extract used in cheese-making. It was also our purpose to learn how the proteolytic action of rennet compares with that of commercial pepsin.

It has been quite generally believed that the rennet extracts used in the manufacture of cheese contain not less than two enzymes or ferments, called rennin and pepsin, one ferment coagulating milk-casein and the other converting milk-casein and paracasein, under favorable conditions, into soluble forms of nitrogen compounds. The present tendency, however, is in the direction of the belief that both kinds of action are due to the presence of only one enzyme. The presence of a proteolytic ferment in rennet extract is readily understood, when we consider its source, which is the stomach of a suckling calf.

For years the weight of opinion was against the belief that rennet has any other function in cheese-making than simply to coagulate milk-casein. In some work[1] done by one of us in 1892, it was shown that cheese, made with larger amounts of rennet, furnished greater quantities of soluble nitrogen com-

[1] New York Agr. Expt. Sta. Bull. No. 54, p. 267 (1893).

pounds than did cheese made with smaller amounts of rennet. In 1899, some additional work[1] was done, confirming the results previously obtained. Babcock, Russell and Vivian[2] have made a very thorough investigation of this subject, showing that, in the case of normal cheese, increased use of rennet resulted in a more rapid increase of soluble nitrogen compounds, especially of those nitrogen compounds grouped under the names of caseoses and peptones. They also made cheese from milk to which purified commercial pepsin had been added and found similar chemical changes taking place in the cheese thus made. They concluded, from these experiments with normal cheese, that rennet exerts a digestive influence on casein, due to the presence of peptic enzymes contained in rennet extracts, the action of which is intensified by the development of acid in the cheese-curd. Jensen,[3] working independently and along quite different lines, reached the same conclusions at the same time.

In the case of the work previously done here and elsewhere, the effect of rennet ferment has not been studied apart from the action of other factors that are present in normal cheese-ripening. So far as our present knowledge goes, the different agencies taking part in the normal process of cheese-ripening are the following: (1) Some acid, usually lactic; (2) enzymes present in the milk before it is made into cheese; (3) an enzyme contained in the rennet extract added to milk in the cheese-making process; and (4) micro-organisms, chiefly bacteria. In previous studies of the effect of rennet ferment on cheese-ripening some or all of these factors have been present, so that the specific action of rennet has had to be inferred rather than been clearly proved. It has been the special aim of our work to study the action of the rennet ferment as far as possible apart from the other agencies of cheese-ripening. Under these conditions, we have studied the action of rennet extracts in cheese-ripening: (1) Without acid, (2) in the presence of acid, (3) without salt, and (4) with salt. In addition, we have studied the action of rennet extracts of different ages upon the casein of milk, and also the proteolytic action of commercial pepsin on milk-casein and in the process of cheese-ripening. We have also studied the action of rennet enzyme and pepsin on paracasein dilactate.

[1] New York Agr. Expt. Sta. Bull., No. 236, p. 150 (1903).
[2] Annual Report, Wis. Expt. Sta., **17**, 102 (1900).
[3] *Landw. Jahrb. d. Schweiz.*, **14**, 197 (1900).

Description of Experimental Work.

DIFFICULTIES INVOLVED IN THE WORK.

In order to destroy all enzymes present in milk, our general plan of procedure has been to heat the milk to a temperature varying in different cases from 85° C. to 98° C. (185° F. to 208° F.). Then, in order to prevent possible contamination by the entrance of enzyme-producing organisms, the milk, after being heated and cooled, has been treated with 3 to 5 per cent. of chloroform by volume, previous to being made into cheese. The heating of milk to the temperature stated diminishes the readiness and completeness with which it is coagulated by rennet extract, but the power of prompt coagulation by rennet can be restored by the addition of calcium chloride or carbon dioxide or any ordinary acid. In thus eliminating other factors of cheese-ripening than rennet enzyme, we necessarily produce conditions that do not exist in normal cheese-making, such as (1) heated milk, (2) absence of milk-enzymes, (3) the use of calcium chloride or carbon dioxide, and (4) absence of enzyme-forming and acid-forming organisms. In a study carried on under such conditions, we cannot expect our results to be entirely comparable with results obtained under normal conditions; but we can secure data that enable us to determine the ability of the rennet enzyme to cause proteolytic changes under the conditions of experiment employed. Later we will inquire as to whether the introduction of such unusual conditions seriously affected the value of the results obtained, in their application to the process of normal cheese-ripening.

EFFECT OF ACID UPON THE PROTEOLYTIC ACTION OF RENNET ENZYME.

Table I contains the averages of results given by four sets of experiments, in which the effect of the presence and absence of acid upon the action of rennet enzyme in cheese-ripening was studied.

TABLE I.—EFFECT OF PRESENCE AND ABSENCE OF ACID UPON THE ACTION OF RENNET ENZYMES.

		Nitrogen, expressed as percentage of nitrogen in cheese, in form of			
Acid.	Age of cheese when analyzed.	Water-soluble nitrogen compounds. Per cent.	Paracasein monolactate. Per cent.	Paranuclein caseoses and peptones. Per cent.	Amides. Per cent.
Present	Fresh	4.55	26.80	3.78	0.77
"	12 mos.	25.85	11.59	20.87	4.98
Absent	Fresh	3.13	1.88	2.73	0.80
"	12 mos.	4.23	1.68	2.26	3.96

A comparison of the data embodied in this table shows a relatively large formation of water-soluble nitrogen compounds in twelve months in the presence of acid, while in the absence of acid practically no proteolysis had occurred. Paracasein monolactate was present in only minute quantities, if at all, in the absence of acid, while a considerable amount was formed in the presence of acid. The increase of soluble nitrogen compounds was confined largely to the paranuclein, caseoses and peptones, the amount of amides remaining small. In normal cheese-ripening, we find these relations reversed, that is, the amides form a considerably larger part of the soluble nitrogen compounds than do the higher groups.

The results embodied in Table I may properly be interpreted as showing that the proteolytic action of the rennet enzyme, in cheese-ripening, is dependent upon the presence of acid.

EFFECT OF RENNET ENZYMES IN CHEESE CONTAINING ACID-FORMING AND SOME PROTEOLYTIC ORGANISMS.

For the purpose of comparison, it was desired to have some cheeses made from milk pasteurized at 85° C. (185° F.). As factors active in causing proteolytic changes, we had in the cheeses made in these experiments (1) acid, (2) rennet enzyme, and (3) such micro-organisms as happened to be introduced with the "starter" and from the air of the room. As compared with a normal cheese, there were no milk enzymes present and the biological factor would be expected to be considerably less marked. In comparison with the cheeses referred to in Table I, we had in these no chloroform, a difference that meant absence of a biological factor in the former case. In these cheeses, the acid was furnished by a sour-milk "starter." In Table II, we give the results of chemical analysis made when the cheese was fresh from the press and when nine months old.

TABLE II.—SHOWING COMPOSITION OF CHEESE MADE FROM PASTEURIZED MILK.

	Nitrogen, expressed in percentage of nitrogen in cheese, in form of				
Age of cheese when analyzed.	Water-soluble nitrogen compounds. Per cent.	Paracasein monolactate. Per cent.	Paranuclein, caseoses and peptones. Per cent.	Amides. Per cent.	Ammonia. Per cent.
Fresh.....	3.13	11.36	3.13	0	0
9 months.....	25.54	5.14	12.79	12.75	1.31

In studying these results, we notice that there was an increase in all the different classes of water-soluble compounds during the period of experiment. The amount of amido compounds was considerably in excess of that noticed in Table I in the case of cheeses made and kept in the presence of chloroform. Ammonia was formed, while none was present in Table I. The increased amounts of amido compounds and the presence of ammonia, observed in these experiments, as compared with the results of the experiments given in Table I, must be ascribed to the presence in the former of a biological factor and not to rennet enzyme.

COMPARISON OF THE EFFECT OF COMMERCIAL PEPSIN WITH THAT OF RENNET ENZYME IN CHEESE-RIPENING.

In the following experiments, the cheeses were made in the normal way, without chloroform, except that the milk was pasteurized at 85° C. (185° F.) and hydrochloric acid was used in the place of lactic acid or a "starter." In 55, rennet extract alone was used at the usual rate of 2.5 ounces for 1000 pounds of milk. In 56, in addition to rennet extract, we added 1 gram of Parke, Davis & Co.'s aseptic scale pepsin dissolved in water, and in 57, we used 15 grams of the pepsin and the usual amount of rennet extract.

TABLE III.—SHOWING EFFECT OF COMMERCIAL PEPSIN IN CHEESE-RIPENING.

No. of experiment.	Age of cheese when analyzed.	Enzymes added.	Nitrogen, expressed as percentage of nitrogen in cheese, in form of: Water-soluble nitrogen compounds. Per cent.	Paracasein monolactate. Per cent.	Paranuclein, caseoses and peptones. Per cent.	Amides. Per cent.	Ammonia. Per cent.
55	Fresh	Rennet extract	4.76	65.45	2.41	2.36	0.0
55	6 mos.	Rennet extract	28.37	17.14	15.87	6.35	2.00
56	Fresh	Rennet and 1 gram pepsin	6.97	36.76	4.11	2.86	0.0
56	6 mos.	Rennet and 1 gram pepsin	29.80	17.04	16.47	7.10	1.91
57	Fresh	Rennet and 15 grams pepsin	25.00	59.53	22.80	2.20	0.0
57	3 mos.	Rennet and 15 grams pepsin	46.67	11.61	41.00	5.68	0.49

In studying the results contained in Table III, we notice:

(1) The use of 1 gram of commercial pepsin in addition to rennet extract slightly increased the proteolytic results in the cheese. This cheese contained considerably less moisture than 55 or 57.

(2) The use of 15 grams of commercial pepsin along with rennet extract produced very marked results. This is strikingly evident in the fresh cheese, where we have 25 per cent. of the nitrogen in the cheese present in the form of water-soluble compounds, while in the case of Experiment 55, in which rennet extract only was used, the amount of soluble nitrogen compounds is less than 5 per cent. At the end of three months, we still have much more of the soluble nitrogen compounds in 57, the pepsin cheese, than we have in 55, the rennet extract cheese, at the end of six months.

(3) In comparing the proteolytic factors in Experiments 55 and 57, the conditions of work were such that the chief essential difference was the presence of pepsin in the latter, though 57 contained more moisture than 55. The observed difference in the chemical results could, therefore, be due only to pepsin, and this would be particularly true of the results obtained in the fresh cheese.

COMPARISON OF THE EFFECT OF RENNET ENZYME AND OF COMMERCIAL PEPSIN IN MILK, WITH AND WITHOUT ACID.

We made a comparative study of the effect of rennet enzyme and of commercial pepsin upon milk-casein and upon casein monolactate. These experiments were carried out in the following manner: We heated 8.6 liters of milk for fifteen minutes at 85° C. (185° F.), and after cooling added 2 per cent. of chloroform by volume. Of this milk, we placed in each of several bottles 100 cc. In one case, we added, to the neutral milk, 0.22 cc. of Hansen's fresh rennet extract, and in another the same amount of old rennet extract. In other bottles, we added, in addition to the rennet extract, 0.5 cc. of pure concentrated lactic acid, which was sufficient to convert the milk-casein into the monolactate. For comparison, we placed in other bottles, with and without acid, the same amount of milk and 0.06 gram of Parke, Davis & Co.'s aseptic scale pepsin for each 7 grams of proteid contained in the milk. Duplicates were used in all cases. The

contents of these bottles were kept at 15.5° C. (60° F.) and were examined at intervals, both chemically and bacteriologically. With the exception of a single determination, in the case of one bottle, the germ content was below 50 per cubic centimeter, which undoubtedly represented spore forms. The old rennet extract was used for the purpose of answering the question as to whether the proteolytic changes, observed in Table I, were due to rennet enzyme alone, or whether the rennet may not have contained some proteolytic bacterial enzymes produced in the rennet extract previous to its use.

The results of chemical analysis are given in the subjoined table. The determinations of nitrogen in the form of amides were made by the use of phosphotungstic acid, since it has been shown[1] that, in the case of peptic digestion, phosphotungstic acid is a more satisfactory reagent than tannic acid, especially in solutions having an acid reaction. The amount of nitrogen originally in the milk was 0.561 per cent.

TABLE IV.—SHOWING THE EFFECT OF RENNET ENZYME AND COMMERCIAL PEPSIN UPON MILK-CASEIN AND CASEIN MONOLACTATE.

Kind of enzyme used.	With or without lactic acid.	Age of milk when analyzed.	Nitrogen, expressed as percentage of nitrogen in milk, in form of		
			Soluble nitrogen compounds. Per cent.	Caseoses and peptones. Per cent.	Amides. Per cent.
.....	.....	Fresh	9.98	....	....
Fresh rennet	Without	1 mo.	11.35	6.00	5.35
" "	With	1 "	29.80	22.22	7.58
Old rennet	Without	1 "	12.57	4.99	7.58
" "	With	1 "	25.23	18.55	6.68
Commercial pepsin	Without	1 "	8.91	2.22	6.69
" "	With	1 "	33.51	25.93	7.58
Fresh rennet	Without	9 mos.	18.98	13.63	5.35
" "	With	9 "	53.57	45.64	7.93
Old rennet	Without	9 "	17.03	12.13	4.90
" "	With	9 "	47.96	39.67	8.29
Commercial pepsin	Without	9 "	10.08	6.51	3.57
" "	With	9 "	56.96	48.05	8.91

The data embodied in Table IV appear to be quite definite in respect to the following points:

(1) The increased activity of rennet extract as well as of pepsin in the presence of acid is very marked. Expressed in another

[1] New York Agr. Expt. Sta. Bull. No. 215, pp. 90 and 98 (1900).

way, these enzymes act upon casein monolactate much more extensively than upon milk-casein.

(2) If we compare the results secured by the use of the purest commercial pepsin with those given by the rennet extracts, we find that, in the presence of acid, there are formed soluble nitrogen compounds quite close in amount to those formed by rennet extract. The amount of soluble nitrogen compounds formed in neutral solution was fairly stationary during the nine months, while, in the case of the rennet extracts, there was a slow increase. The amount of amido compounds was surprisingly uniform in the case of the pepsin and the rennet extracts, in both neutral and acid reaction.

(3) At any given time, the fresh rennet extract had, in most cases, formed a larger amount of soluble nitrogen compounds than had the old extract. This was particularly true in acid solution. This result does not indicate that we had bacterial enzymes in the old rennet in addition to rennet enzyme. The difference in action of the two rennet extracts is not marked in the class of amido compounds. If the old extract contained bacterial enzymes, we should expect it to produce larger amounts of amido compounds. These results fail to show that the old rennet extract contained any proteolytic bacterial enzymes, as compared with the fresh extract. Moreover, the results given by pepsin suggest that the pepsin was able to account for all the changes observed in the case of the rennet extracts in the presence of acid.

COMPARISON OF THE EFFECT OF RENNET ENZYME AND OF COMMERCIAL PEPSIN ON PARACASEIN DILACTATE.

Paracasein monolactate was extracted from several pounds of cheese by a 10 per cent. solution of sodium chloride and this was treated with acid, precipitating paracasein dilactate. Of this compound washed free from salt, we placed 25 grams, suspended in water, in each of several flasks and sterilized by heat. We then sterilized some solution of pepsin and rennet extract by treating with 0.5 per cent. of formalin, containing 0.2 per cent. of formaldehyde. According to Bliss and Novy,[1] pepsin is not affected by a 1 per cent. solution of formaldehyde nor rennet by a 4 per cent. solution. In one set of flasks, we added to each

[1] *Jour. Expt. Med.*, **4**, No. 1 (1899).

0.06 gram of the sterilized pepsin, and in each of the other set of flasks 0.5 cc. of the sterilized rennet extract. Duplicates were used in all cases. These were examined bacteriologically and chemically, at intervals for three months. The formalin was very effective in destroying bacterial forms. In some cases a few molds were found, but not in sufficient number to affect the work. The nitrogen in the material was 4.35 per cent.

TABLE V.—SHOWING EFFECT OF RENNET ENZYME AND COMMERCIAL PEPSIN ON PARACASEIN DILACTATE.

		Nitrogen, expressed as percentage of nitrogen in mixture, in form of				
Enzymes used.	Age when analyzed.	Water-soluble nitrogen compounds Per cent.	Para-casein mono-lactate. Per cent.	Para-nuclein caseoses and peptones. Per cent.	Amides. Per cent.	Ammonia. Per cent.
Pepsin	2 weeks	33.68	2.30	....	....	0
Rennet	"	34.95	2.30	....	....	0
Pepsin	1 mo.	41.61	...	37.87	3.74	0
Rennet	"	43.68	...	40.00	3.68	0
Pepsin	3 "	55.75	...	46.55	9.20	0
Rennet	"	57.25	...	49.53	7.72	0

From the data contained in Table V, we can see that the results of our work indicate that:

(1) Both pepsin and rennet enzyme exerted a marked proteolytic effect upon the paracasein dilactate, digesting about one-third of it in two weeks and considerably over one-half in three months. While the rennet enzyme appears somewhat more active in forming water-soluble nitrogen compounds, the actual difference is small.

(2) Both enzymes formed amides in small quantities, but neither produced any ammonia.

(3) If we compare the results in Table V with those in Table III, we find that more proteolysis occurred in this experiment than in the presence of chloroform. This is true of both enzymes. This suggests that the chloroform may exert a retarding influence upon the action of pepsin and rennet. Malfitano[1] makes the statement that the action of pepsin is considerably diminished by chloroform. The difference noted in our work may be due to the greater amount of acid present in the experiment in Table V. However, both sets of experiments practically agree in showing small formation of amides and entire absence of ammonia.

[1] *Ann. Inst. Pasteur*, **16**, 853 (1902).

EFFECT OF COMMON SALT ON THE ACTION OF RENNET ENZYME IN CHEESE-RIPENING.

Previous work[1] shows that salt exerts a marked repressing influence upon the proteolytic action of those enzymes that are present in milk when made into cheese. We have also found that in normal cheese the addition of increased quantities of salt decreases the rapidity of proteolysis. We planned several of our experiments with a view to study the action of salt on cheese-ripening, when rennet enzyme is the only proteolytic factor present. The results were not at all conclusive, but seem to indicate, as far as they go, that, in cheese-ripening, salt, in the proportions commonly used, has little or no influence upon the action of rennet enzyme. It may be mentioned, in this connection, that Chittenden and Allen[2] have shown that the action of pepsin, in digesting blood-fibrin, is diminished by the presence of common salt.

EFFECT OF ABNORMAL CONDITIONS PRESENT.

We have already called attention to the difference of conditions present in the experiments described in this bulletin and those found in normal cheese. We will now consider these in more detail. These abnormal conditions, found in our experiments, but not present in normal cheese, are the following: (1) Milk heated to 85° C. to 98° C. (185° F. to 208° F.) to destroy all enzymes originally existing in milk; (2) the use of calcium chloride or carbon dioxide gas to restore the coagulating property of milk-casein by rennet extract; and (3) the use of chloroform to suppress all activity of organisms. The question naturally arises as to whether the introduction of these unusual conditions seriously affected the results obtained and, if so, in what manner and to what extent.

If the conditions mentioned showed any influence upon the action of rennet enzyme, the tendency was an unfavorable one for the action of this enzyme.

SUMMARY AND DISCUSSION OF RESULTS.

In the work described in the preceding pages, we have studied the proteolytic action of rennet enzyme under the following conditions:

[1] New York Agr. Expt. Sta. Bull. No. 203, p. 241 (1901).
[2] "Studies in Physiological Chemistry," Yale Univ., I, 92 (1884–'85).

(1) *In Cheese Containing Rennet Enzyme as the Only Proteolytic Agent, with and without Acid, and also with and without Salt.*—In these experiments, all milk-enzymes were destroyed by heating at 95° C. to 98° C. (205° F. to 208° F.); the coagulable property of the milk-casein was restored by the addition of either calcium chloride or carbon dioxide gas, and all organisms were rendered inactive by chloroform. Acid, when present, was furnished by addition of pure lactic acid.

(2) *In Cheese Containing Rennet Enzyme together with Acid-forming and Some Proteolytic Organisms.*—In these experiments, the milk-enzymes were destroyed by heating, acid was furnished by a lactic acid "starter," but no chloroform was used. We thus had, as our only proteolytic agents, rennet enzyme in the presence of acid and some liquefying organisms that were introduced in the "starter" or that got into the milk or curd during the operation of cheese-making.

(3) *In Cheese Containing Commercial Pepsin in Addition to Rennet Enzyme, together with Hydrochloric Acid and Such Organisms as Were Introduced during the Process of Making Cheese.*—In these experiments, the milk enzymes were destroyed by heat and commercial pepsin added in different amounts.

(4) *In Comparison with Commercial Pepsin on Casein in Milk, with and without Acid.*—In these experiments, the milk enzymes were destroyed by heat and all organisms were rendered inactive by chloroform.

(5) *In Comparison with Commercial Pepsin on Paracasein Dilactate.*—In these experiments, rennet enzyme and commercial pepsin, sterilized by formaldehyde, were allowed to act upon sterile paracasein dilactate.

The results of these experiments appear to us to justify the following statements:

(1) In the case of every experiment made, whether with cheese or milk, there was little or no proteolytic action of either rennet enzyme or commercial pepsin in the absence of acid, while there was marked action, though in varying degrees, in the presence of acid.

(2) In the absence of acid in cheese, no paracasein lactate is formed and little or no proteolysis occurs; in the presence of acid in cheese, or more strictly in the milk and curd, paracasein mono-

lactate is formed and proteolysis takes place, with the rennet ferment as the active agent. The ability of rennet enzyme to convert paracasein into soluble nitrogen compounds appears to depend upon the presence of paracasein lactate. In cheese-making, therefore, the primary function of acid appears to be the formation of a chemical compound with paracasein, commonly paracasein monolactate but, in excess of acid, paracasein dilactate. The conversion of paracasein monolactate by rennet enzyme into soluble nitrogen compounds is strongly suggested by the fact that, when the soluble nitrogen compounds increase, the paracasein monolactate decreases.

(3) In comparing rennet enzyme and commercial pepsin in the case of cheese, milk and paracasein dilactate, the experiments that were strictly parallel have shown about the same extent of proteolytic action.

(4) In the case of both rennet enzyme and commercial pepsin, the chemical work performed by the ferments is confined mainly to the formation of paranuclein, caseoses and peptones, while only small amounts of amides are formed, and no ammonia.

(5) Rennet enzyme is a peptic ferment, as shown by the following characteristics: (*a*) Neither rennet enzyme nor pepsin causes much, if any, proteolytic change, except with the help of acid; (*b*) the quantitative results of proteolysis furnished by rennet enzyme and pepsin agree closely when working on the same material under comparable conditions; (*c*) the classes of soluble nitrogen compounds formed by the two enzymes are the same both qualitatively and quantitatively; (*d*) neither enzyme forms any considerable amount of amido compounds, and neither produces any ammonia; (*e*) the soluble nitrogen compounds formed by either enzyme are chiefly confined to the groups of compounds known as paranuclein, caseoses and peptones.

(6) The experiments made to determine the influence of salt on the proteolytic action of rennet enzyme, while not conclusive, suggest that salt has little or no effect upon the action of rennet enzyme in cheese-ripening.

(7) In obtaining our results relating to the study of the function of rennet enzyme in cheese-ripening, we were necessarily compelled to work under conditions more or less abnormal as compared with the conditions commonly present in cheese-

making. The effect of such unusual conditions would tend, if they had influence at all, to diminish the proteolytic action of rennet enzyme. We are, therefore, justified in believing that our results represent the minimum effect of rennet enzyme in cheese-ripening and that, under normal conditions, it takes, if anything, a larger part than that indicated by our experiments.

(8) In some experiments, we eliminated all milk enzymes and all active forms of organisms contained in the milk before making it into cheese. In some cases, we had rennet enzyme in the presence of acid as the only proteolytic agent in the cheese; in others, we had the same conditions and, in addition, such proteolytic organisms as chanced to get into the milk and curd during the process of cheese-making. In the latter case larger amounts of amides were formed, and some ammonia, while, in the presence of rennet enzymes alone, no ammonia was formed and only small amounts of amido compounds. When we compare normal cheese with cheese containing only rennet-enzyme, we find the same difference, except that it is more pronounced, as we should expect. Hence, the special work done by the rennet enzyme as a factor in cheese-ripening is that of a peptic digestion, forming groups of water-soluble nitrogen compounds, intermediate in complexity of structure between paracasein and the amido compounds, *viz.*, paranuclein, caseoses and peptones.

In normal cheese, we find an accumulation of amides and ammonia, as the cheese grows older and a corresponding diminution of the compounds previously formed. The formation of all the ammonia and of a large proportion of the amides found in ripened cheese must be due to some agency other than rennet enzyme, and the only other agents present, besides milk enzymes, that can do this work appear to be organisms or their enzymes. The first stage in normal cheese-ripening is essentially a peptic digestion of paracasein monolactate. Gradually amides are formed and later ammonia. It is probable that the first chemical work done in normal cheese-ripening is the conversion of paracasein monolactate by rennet enzyme into paranuclein, caseoses and peptones. The question naturally arises as to whether these compounds must be formed before other agents can take part in the work and carry it along farther, producing amides and ammonia. We are at present engaged in studying this phase of the problem.

(9) When rennet enzyme was the only digesting agent in cheese, we were unable, in any case, to find the slightest traces of cheese flavor. Apparently, we must look to other sources for this important product of cheese-ripening.

NEW YORK AGRICULTURAL EXPERIMENT STATION, GENEVA N. Y.

A METHOD OF GRADING SOAPS AS TO THEIR DETERGENT POWER.

BY H. W. HILLYER.

Received October 7, 1903.

AS FAR as known to the writer, no method for directly determining the detergent value of a soap is now known. It is assumed, and with much justice, that the value of a soap is a function of the amount of combined fatty acids present, and the valuation of soaps is now based on the determination of the fatty acids. Besides this, the determination of the free alkali and of water and various filling materials is required. These determinations give evidence on which the valuation of the soap may be based and, to some extent, for ascertaining the materials from which it is made, but do not give any direct measure of the value as a cleansing agent and, further, require a complex judgment to interpret them.

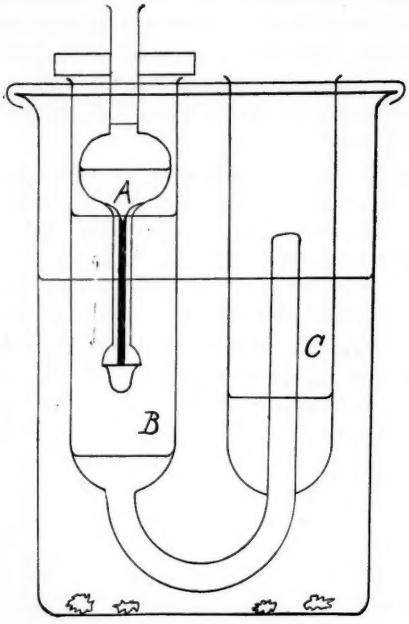
The method now proposed is based on the study of sodium soaps, previously publishd in this Journal, **25**, 511 and 524. In the articles indicated, it was found that when a solution of a soap is made to form drops beneath the surface of an oil, the number of drops formed from a given volume of the solution is dependent on the amount of soap present in the solution. Further, the conclusion was reached that the number of drops formed was a measure of the emulsifying power of the given soap solution, and that the emulsifying power was so large a part of the cleansing power that it might stand as a measure of it, especially, since two of the other probable factors in cleansing, namely, penetrating or wetting power, and lubricating power are dependent on the same physical properties as the emulsifying power.

Soaps are used principally in one of two ways. They are used with cold or luke-warm water, as in wool-scouring and for toilet purposes; or, on the other hand, they are used in boiling water, as in silk-boiling, dish-washing, and laundry work. A soap may be of value for one of these purposes and of comparatively little value for the other. The method proposed takes these two peculiar conditions of use into account and attempts to grade the soaps as to their efficiency for cold use and, on the other hand, for use with hot water.

For making the test for efficiency in use with hot water, the apparatus is similar to that used for the study of sodium palmitate and stearate, but modified in the interest of greater constancy of results. The essential part is a pipette (A) with a capillary outlet of about 0.5 mm. internal diameter and a flat, horizontal surface, about 10 mm. in diameter, from which the drops fall. This surface must be free from capillary openings, which may contain air, as described in a former article. The reservoir of the pipette is spherical, that it may have a small vertical height relatively to its volume, since a great vertical height makes a greater difference in the pressure and consequent rate of flow at the commencement and at the end of an observation. When the initial pressure is great, the rapidity of flow may make the solution run down in a stream or cause the drops to be formed too rapidly to be easily counted. This may be overcome by dipping the pipette more deeply into the oil; but when that is done the later drops are formed more slowly than is desirable. By having the bulb capacious in proportion to its vertical height the initial and final rates of flow are nearly enough alike to prevent any special difficulty. The pipette holds 5 cc. from a mark on the stem to the upper end of the capillary. The stem has an internal diameter of 3 mm., wide enough to allow filling from above, and, to facilitate this method of filling, it is widened at the upper end into a small funnel.

The second part of the apparatus is the receptacle for the oil, which may be a simple test-tube, but is preferably made in the form (BC) indicated in the drawing. This form maintains a more nearly constant pressure and promotes more regular work. To maintain the apparatus at the boiling-point of water, it is supported in a large beaker, which is used as a water-bath. The

beaker is covered with a sheet of zinc or aluminum with its edges turned down over the edge of the beaker, and with a perforation cut in it suitable for the insertion of the apparatus.



To make use of the apparatus, 2 or 3 cc. of water are poured into B and then followed by 20 cc. of kerosene. A little of the solution to be tested, previously heated on a boiling water-bath, is poured into the pipette and shaken about, and then blown out through the capillary, using a piece of rubber tubing as a mouth-piece. This is repeated twice more. Then the pipette is filled full, and by a strong pressure from the lungs the air bubbles are forced out of the capillary and washed away. The pipette, supported in a cork, is placed in the kerosene, and the number of drops formed from 5 cc. of the solution is counted. The solution, as it flows from the pipette, falls to the bottom of the oil reservoir B and overflows into C, while the level of the kerosene remains constant and the variation of pressure is that only which results from the change of level of the solution in the pipette.

Since this is in every case the same, comparable results are more easily obtained than by the use of a test-tube as oil reservoir.

To make a test of efficiency of the soap for use in cold water, the same apparatus is used, except that the beaker, used as a water-jacket, is not necessary.

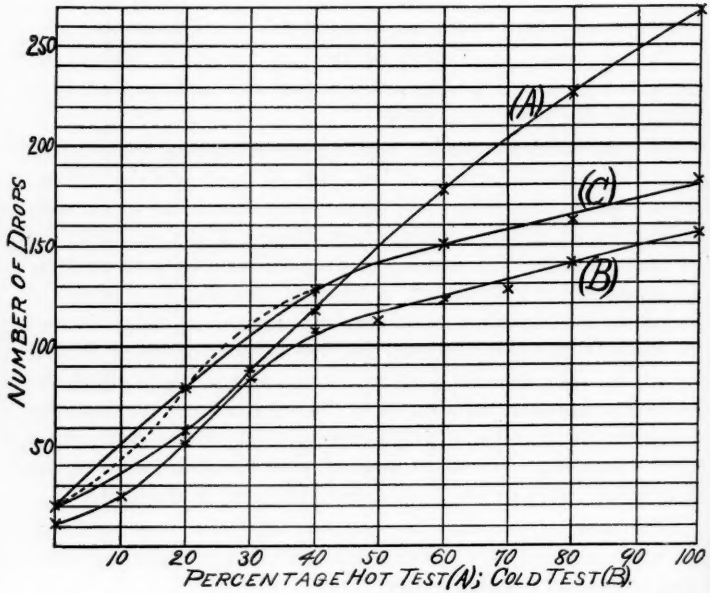
As a standard for the hot test, 1 gram of neutral sodium palmitate, dissolved in 200 cc. of hot water, is used. Of this, 10 cc., 20 cc., 30 cc., and 40 cc. are, respectively, diluted to 50 cc. with boiling water, giving solutions containing 0.2, 0.4, 0.6, and 0.8 of the standard. The number of drops formed by each of these solutions, when it flows into a kerosene, adopted as a standard kerosene, is determined, and also the number of drops formed by the standard solution itself and the number of drops formed by water. The data obtained are plotted as a curve in which the ordinates represent percentages of the standard and the abscissas represent the number of drops corresponding to the percentages of the standard. The data, obtained with a certain kerosene, are here given and the curve (A) derived is shown in the figure.

The standard is made by bringing together 0.921 gram of palmitic acid and 36 cc. decinormal sodium hydroxide and diluting to 200 cc. with hot water.

Full standard gives drops				271–265–269	= 268	average.
0.8	"	"	"	228–228	= 228	"
0.6	"	"	"	180–178	= 179	"
0.4	"	"	"	118–121	= 119	"
0.2	"	"	"	56–55½	= 56	"
Water		"	"	19	= 19	"

If any solution of sodium palmitate, which contains an amount less than one part in 200 of water, is tested by the dropping method at the boiling-point, the amount present may be determined by counting the number of drops formed. By finding, on the curve, a point corresponding to the number of drops counted and letting fall a perpendicular from this point upon the base line, a point will be found which indicates, as a percentage of the standard, the amount of palmitate present.

Other soaps may be tested in the same way and referred to sodium palmitate as a standard. If 0.5 gram of a commercial soap is dissolved in 100 cc. hot water and its solution tested at the boiling-point, we may state the result in this way: The soap



in question gives the number of drops which would be given by a solution of sodium palmitate containing (x) per cent. of the standard.

According to the conclusions arrived at in the previous articles, the number of drops is a measure of the detergent power of the solution. Consequently, the result of the test may be stated as follows: The soap has, when used for cleansing with hot water, a detergent power as great as a soap containing (x) per cent. of sodium palmitate.

TEST FOR COLD-WATER SOAPS.

A solution containing one part of sodium oleate in 200 parts of cold, freshly boiled, distilled water is taken as the 100 per cent. standard for soaps to be used with cold water. From this, fractional standards are made as before, using cold, freshly boiled, distilled water to dilute with. All are tested as to their drop number in the cold and a curve constructed. In a previous article it was stated that the curve for sodium oleate was differ-

ent in shape from the curves for the other sodium soaps tested. The following data gives a curve for oleate (B), which appears to have nearly the same form as the curves previously given for rosin soap and different from the curves formerly given for oleate. But this difference is due to the greater dilution of the solution and to the greater number of fractional standards, and to the fact that observations are made nearer the origin. The curve shows that sodium oleate is somewhat hydrolyzed at great dilutions. A set of standards gave the following data and curve (B).

Full standard gives drops			153–153 = 153	average.
0.8	"	"	139–141 = 140	"
0.7	"	"	128–128 = 128	"
0.6	"	"	123–122 = 123	"
0.5	"	"	111–111 = 111	"
0.4	"	"	107–105 = 106	"
0.3	"	"	84 = 84	"
0.2	"	"	51–50 = 51	"
0.1	"	"	25–25 = 25	"
Water		"	11–11 = 11	"

For evaluating a commercial soap for efficiency in use with cold water, the following method of working was decided upon after trying several others, which will be indicated later. The soap to be tested is shaved as thin as possible, and 0.5 gram of the shavings weighed and placed in a 100 cc. flask. The flask is then filled to the mark with cold, freshly boiled water and allowed to stand over night. In the morning the solution is stirred, and filtered through a dry filter, letting all run through that will and keeping the solution in the funnel protected from the carbon dioxide of the air by a watch-glass. When all has run through, the filtrate is stirred gently, avoiding making a foam, and a dropping test in the cold is made, using the same pipette and kerosene as that used in testing the standards. By applying, to the standard curve, the drop number observed, a number is obtained which may be stated, as in case of the hot test. A certain number of drops shows that the soap in question is as efficient for cold cleansing as an equal amount of soap containing (x) per cent. of sodium oleate.

Since surface-tension, viscosity, specific gravity and solubility, factors which enter more or less into the working of the test, are all influenced by changes of temperature, it is best to maintain

the temperature constant, as nearly as possible, in all the work involved in making the cold test. It will be convenient, in many cases, to select a convenient room temperature and maintain this, as nearly as possible, during the preparation and testing of the standards, and the preparation and testing of the soap solutions to be evaluated. If many tests are to be made, a trough with glass sides, through which a stream of hydrant water is maintained, might be convenient to set the flasks in and to receive the oil-holder while observations are being made.

Data obtained with a few commercial soaps are here given, showing for each the number of drops formed in the cold test and the percentage efficiency for cold use, indicated by the test; and the drop number by the hot test and percentage efficiency for hot use. The soaps tested are nearly all much-advertised soaps.

	Cold.		Hot.		
Number.	Drops.	Efficiency.	Drops.	Efficiency.	Remarks.
1	121	37	90	31	Cold made, cocoanut oil.
2	56	13	67	21	Hygienic cocoanut oil.
3	114	34	221	77	Toilet.
4	119	36	202	69	Shaving.
5	84	22	80	28	Tar, toilet.
6	75	19	103	35	Yellow laundry, rosin.
7	100	28	135	45	" " "
8	107	31	173	58	Household for cold use.
9	98	27	150	50	" " "
10	139	49	170	57	" " "
11	97	27	206	71	White laundry and toilet.
12	...	..	226	79	" "
13	...	..	216	75	Prime yellow laundry.
14	120	37	218	76	" " "
15	104	30	277	106	Steam laundry, tallow.
16	142	54	...	...	Castile, old and dry.

These results show how wide a difference there is between soaps which have wide sale and also the desirability of having some standard by which to readily judge them. In the retail market, many household soaps sell at the price of five cents per bar. The bars vary very much in weight, but it was found that in a number of cases the value per bar was approximately equal according to the dropping test. For example, No. 6 is sold in bars weighing 330 grams; its hot test shows 35 per cent. The product of these, or efficiency per bar is 115.5. No. 7 is sold in

270-gram bars. The hot test shows 45 per cent., or efficiency per bar, 121.5. No. 11 is sold in 160-gram bars. Hot test, 71 per cent. Efficiency per bar, 113.6.

This calculation shows that in some cases the manufacturers have correctly estimated the relative value of their product.

From the table it may be seen that those soaps intended for toilet purposes or advertised for cold use are, for the most part, of a relatively high efficiency by the cold test. No. 16 is a dry, old, standard castile soap and shows the highest cold test of any. But it is somewhat surprising that even this is only a little more than half as efficient as pure sodium oleate.

No. 15 is a soap known to be made from tallow. It is consumed by local steam laundries and regarded by them as the best soap they can find for their purpose. According to the hot test, it is above the standard palmitate in efficiency. Nos. 11, 12, 13, and 14 are among the most highly appreciated family soaps on the market, and show a high hot test.

That there is not a complete agreement between the tests and the advertised uses is not strong evidence against the test. The makers may be mistaken in their judgment of the best way to use their soaps, or they may, in some cases, purposely advertise them for uses to which they are not well adapted.

It is not expected that the method, at least in its present form, will give a very exact measure of the value of soaps, but it is hoped that, in a field where there is no exact method, the one here proposed may aid consumers in selecting soaps fitted to their special needs and in writing specifications by which soaps may be contracted for. It is also hoped that it may lead to a more concordant judgment, on the part of manufacturers, as to what a normal soap is, and as to how far it is legitimate to vary from this normal soap. If some ready method of judging a soap is adopted, it may seem unprofitable both to maker and consumer to pay freight charges on water and fillers which are of no real detergent value.

The hot test may be relied upon to give results concordant within 1 per cent. for successive samples and within a much closer limit in duplicate tests of the same sample. The cold test is not as accurate as the hot test on account of the colloidal

nature of the solution. It will probably grade soaps within 4 or 5 per cent. in the case of soaps whose solutions are very slimy, and within a closer limit in cases in which the solutions are mobile.

The working out of the hot test presented no particular difficulty, since the soaps worked with dissolve in hot water to give mobile solutions which readily flow through the pipette and can be readily duplicated. In working out the cold test, the method indicated was adopted only when other methods proved unsatisfactory. It is thought best to give an account of some of these attempts that others may not find it necessary to repeat them without modification.

At first the solutions, prepared for the hot test, were allowed to cool, then poured upon a filter and the filtrate tested cold. But the first portion of the filtrate gives a lower drop number than the later portions, and even if all is allowed to drain off before testing, and in this way an average for the whole sample obtained, the drop numbers for successive samples is not at all concordant. These difficulties are probably due to the great variation in the solubility of the colloidal precipitate which separates, with small differences in temperature and to the slowness with which equilibrium is reached between the dissolved and undissolved colloid.

It was thought that by making the solutions more dilute, they might have a low enough viscosity, when cold, to flow through the pipette without filtering. This was found to be the case when the solutions contained only one part in 400 parts of water, but on testing several soaps of different classes in this way, they all showed nearly the same cold test and no comparison could be based on the results.

Another attempt was made by adding a solution of common salt to the soap solution and then filtering. It was found that when equal quantities of 2.5 per cent. sodium chloride solution were added to 0.5 per cent. sodium palmitate solution, that nearly all of the palmitate was precipitated and the filtrate showed only a small drop number. When the same salt solution was added to 0.5 per cent. oleate solution there was, at first, no precipitation and the drop number was *increased*. But the oleate solution with salt, on making successive tests, showed a rapidly decreasing drop number, making it impossible to use this mixture as a basis

for a standard curve. The decrease in number of drops is very soon apparent, the solution becomes cloudy, and, in a few days, nearly all of the oleate appears to be precipitated, while the filtrates, no matter what the original strength, show a strong tendency to the same minimum drop number.

LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY OF WISCONSIN,
June, 1903.

A RAPID METHOD FOR THE DETERMINATION OF SULPHUR IN COAL AND COKE.

BY J. D. PENNOCK AND D. A. MORTON.

Received October 5, 1903.

As is well known, foundrymen require coke containing a minimum percentage of sulphur. It has been found necessary to be able to quickly determine the percentage of sulphur in the coal to be used for coke-making in order that a selection of those cars containing coal low in sulphur, may be made, for the railroad companies charge demurrage on all cars not emptied in twenty-four hours. By the method described in this paper, one chemist has been able to make twenty determinations of sulphur in six hours.

The determination of sulphur in coals and cokes, as described in this paper, is, in its essential features, a combination of parts of two methods already in use. These parts are, first, the process used by Sundstrom[1] for the complete oxidation of coals by means of sodium peroxide; second, the method of Andrews[2] for the volumetric estimation of the sulphur thus formed.

In carrying out these processes, however, various modifications have been introduced in order to accomplish, as perfectly as possible, the end in view; namely, the accurate, rapid, and convenient estimation of sulphur in coals and cokes. This object is satisfactorily accomplished by following the method as outlined below.

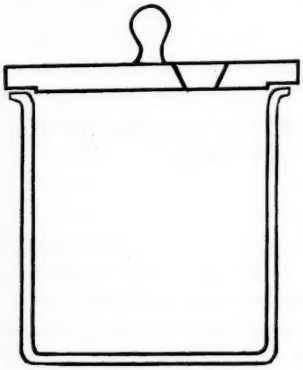
APPARATUS AND SOLUTIONS.

Crucible.—A soft steel crucible of about 40 cc. capacity, the lid being perforated with a small hole for the introduction of the igniting wire.

[1] This Journal, February, 1903.
[2] *Am. Chem. J.*, **11**, 567; *J. Anal. Chem.*, **4**, 73 (1890).

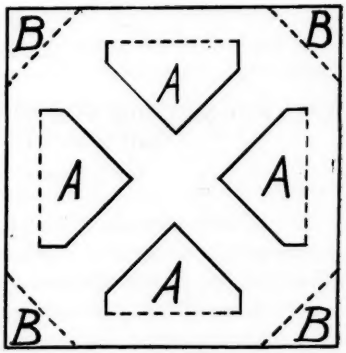
Crucible Stand.—Any arrangement suitable for holding the crucible firmly in place and out of contact with the beaker during the peroxide combustion.

The following diagrams show the form of crucible and stand used in this laboratory:



Crucible.

Thickness of walls and bottom of crucible, $1/32$ inch.
Hole in cover, diameter at top, $1/4$ inch.
Hole in cover, diameter at bottom, $3/32$ inch.
Other dimensions as shown in diagram. The crucible and lid are nickel-plated.



Stand.

The stand is made from a sheet of aluminum, 2 inches by 2 inches, cutting as indicated by the heavy lines, then bending upward at right angles the four points marked "A," and downward at right angles the four points marked "B," making the bends along the dotted lines.

Barium Chromate Solution.—A solution of 23 grams pure barium chromate in a mixture of 80 cc. concentrated hydrochloric acid and 920 cc. water. With the use of commercial C. P. barium chromate, much trouble has been experienced because of its impurity. A suitably pure barium chromate may be prepared by adding a dilute potassium chromate solution to the theoretical quantity of barium chloride, also in dilute solution, and then washing the precipitate thoroughly.

Sodium Thiosulphate Solution (tenth-normal).—24.8 grams of the pure crystallized salt dissolved in water and the solution diluted to 1 liter.

Iodine Solution (tenth-normal).—12.69 grams iodine dissolved in a solution of 18 grams potassium iodide in 50 cc. water and the mixture diluted to 1 liter.

Starch Solution.

THE DETERMINATION.

Introduce into the crucible 16 grams sodium peroxide and 0.7 gram coal (or 11½ grams sodium peroxide and 0.7 gram coke), and mix thoroughly by means of a small spatula. Cover, and place the crucible on its stand in a 20-ounce beaker of water, in such a way that the lower half only is immersed and the base of the crucible is slightly raised from the bottom of the beaker. Ignite the contents by thrusting a red-hot wire through the hole in the cover into the mixture. Complete fusion and combustion take place almost instantaneously. After three minutes or more, remove the stand and tip the crucible over on its side in the water. The fusion dissolves in a few moments and the crucible is then rinsed and removed. Add hydrochloric acid to the solution until distinctly acid, and boil. To the boiling liquid add ammonia until a few drops in excess, let boil vigorously a minute or two, then add 15 cc. of barium chromate solution and boil another minute. Add sufficient water to the boiling solution to make its volume 200 cc., then ammonia until several drops in excess, and continue boiling vigorously for one or two minutes longer. Allow to settle a few moments, filter and wash the precipitate twice thoroughly, using from 20 cc. to 30 cc. of hot water for each washing.

Add about 1 gram potassium iodide crystals to the filtrate, cool to 30° C., add 5 cc. hydrochloric acid, then run in the thiosulphate solution until the end-point is reached. The presence of a few cubic centimeters of starch solution renders the end-point more distinct. Titrate back, if necessary, with the iodine solution.

$$\text{cc. N/10 } Na_2S_2O_3 \times 0.153 = \text{per cent. S.}$$

The determination depends, of course, on the fact that the precipitation of barium sulphate liberates an equivalent amount of chromic acid, which remains in solution as ammonium chromate when the excess of barium chromate is precipitated by ammonia.

REMARKS.

The directions for the peroxide combustion should be followed with especial care, for, if less sodium peroxide is used than the directions require, the reaction may be explosively violent; and, on the other hand, if too much sodium peroxide is used, the combustion will be incomplete. Also, the thorough mixing of the

fuel with the peroxide must not be neglected or an explosive and incomplete reaction will result.

After each addition of ammonia, the solution is boiled to remove most of the excess, but it should still remain slightly ammoniacal. The addition of the barium chromate does not always precipitate the sulphate immediately, but the subsequent boiling for one or two minutes insures complete precipitation. The final washing of the precipitates, if carried too far, will dissolve precipitated chromate and thus introduce an error. It has been found that two washings, using a small amount of hot water for each, produces the desired effect of thoroughly removing the chromate in solution without decomposing the precipitate.

RESULTS.

Up to the present time more than 1000 determinations by this method have been made in this laboratory. The accuracy of the results has been tested by comparison with the Sundstrom method, with the Eschka method, and by tests on solutions of known sulphate content. A number of the results thus obtained are cited below. The determinations on coal sample No. I were made independently by three analysts, each making two tests by the volumetric and two by the Eschka method. The four volumetric determinations of coke sample No. I required exactly one hour's time, showing the extreme rapidity as well as the accuracy of the method.

	Soft coal samples.				Coke samples.	
	I.	II.	III.	IV.	I.	II.
Per cent. S, volumetric method.	1.95 2.03 1.97 1.98 2.01 2.04	1.26 1.26 1.30	1.16 1.16	1.06 1.06 1.02	0.71 0.70 0.70 0.75	1.43 1.41
Per cent. S, Eschka method.	2.03 2.06 2.04 2.06 2.04 2.00	1.30	1.20	1.05 1.07	0.75 0.68 0.70 0.70	
Per cent. S, Sundstrom method.						1.47 1.42

Solutions, each containing 23 grams sodium chloride, a little iron, and a known quantity of sulphate (hence practically of the same composition as the solution obtained by the peroxide fusion of a coal) gave the following results:

Per cent. S present	0.46	0.914	1.37	2.29	0.98	1.96
Per cent. S found.....	0.45	0.91 0.90 0.92	1.35	2.33 2.36	0.96 1.02 0.99 0.99	1.93

CONCLUSION.

The results of all tests show that the method carried out in accordance with the above directions, is accurate to within a few hundredths of a per cent., and is so rapid that an average of two or even three complete determinations per hour can be accomplished. It can be used with especial advantage where large numbers of sulphur determinations are required, since in such a case its saving in time and in the use of platinum becomes an important item.

The method can be successfully employed not only for the determination of sulphur in coals, but also, with suitable modifications, for the determination of small percentages of sulphur in a large number of organic and inorganic substances.

LABORATORY OF THE SOLVAY PROCESS CO.,
SYRACUSE, N. Y.

ON TRIPHENYLMETHYL ACETATE.

BY M. GOMBERG AND G. T. DAVIS.

Received October 12, 1903.

HEMILIAN,[1] the discoverer of triphenylcarbinol, observed that the carbinol reacts with acetyl chloride, giving rise to hydrochloric acid and a crystalline mass which, on exposure to moist air, loses acetic acid and changes back to the carbinol. With acetic anhydride and with benzoyl chloride he obtained unstable esters, which were readily decomposed by water and by alcohol. Later, Allen and Kölliker[2] described a method for the preparation of triphenylmethyl acetate, which consisted in the action of acetyl chloride upon triphenylcarbinol ethyl ether,

$$(C_6H_5)_3C-O-C_2H_5 + CH_3COCl = (C_6H_5)_3C-O-OCCH_3 + C_2H_5Cl.$$

They claim to have identified the escaping gas as ethyl chloride, and give the melting-point and the solubilities, as well as the

[1] *Ber. d. chem. Ges.*, **7**, 1207 (1874).
[2] *Ann. Chem.* (Liebig), **227**, 116 (1885).

analysis, of the acetate. Recently, Herzig and Wengraf,[1] in connection with their studies on the acetyl derivatives of aurin, rosolic acid and benzaurin, repeated the experiments described by Hemilian, and by Allen and Kölliker in regard to the acetyl compound. Herzig and Wengraf find that the acetyl derivative, as obtained by them, possesses greater stability than ascribed to it by Hemilian. They also claim that the original method of Hemilian, the action of acetyl chloride directly upon the carbinol, is to be preferred to the method of Allen and Kölliker, who employed the triphenylcarbinol ethyl ether instead of the carbinol itself. Hemilian, as well as Herzig and Wengraf, concluded that the product described by them was the acetyl derivative, because, on treatment with water, the carbinol was regenerated, apparently by saponification. With alcohol, the acetyl compound gave the triphenylcarbinol ethyl ether, the reaction being the reverse of that which gave Allen and Kölliker the acetyl derivative,

$$(C_6H_5)_3C-O-OCCH_3 + C_2H_5OH = (C_6H_5)_3C-O-C_2H_5 + CH_3COOH.$$

It is on the basis of the above-mentioned researches that the statements in the literature[2] in regard to triphenylmethyl acetate are made. In the following pages it will be shown that the reactions described by the different investigators lead, not to the formation of the acetyl derivative but simply to that of triphenylchlormethane; that the acetyl compound, prepared by us by an indirect method, possesses properties different from those assigned to it by others, and that the acetyl compound could not exist under the conditions of the experiments which were used for its preparation.

Action of Acetyl Chloride.—One of us reported[3] that by treating triphenylcarbinol ethyl ether with acetyl chloride pure triphenylchlormethane was obtained. The discrepancy between these results and those of Allen and Kölliker, who claimed to have obtained, by this reaction, triphenylmethyl acetate, necessitated a careful revision of the experiments.

[1] *Monatsh. Chem.*, **22**, 612 (1901).

[2] "Beilstein," II, 1083; V. Meyer u. P. Jacobson, "Lehrbuch," II, **2**, 109; "Richter," 3rd Ed., 353; Remsen's "Organic Chemistry," 355; Baeyer u. Villiger: *Ber. d. chem. Ges.*, **35**, 3015, etc.

[3] This Journal, **24**, 618 (1902).

(1) The ethoxy compound, $(C_6H_5)_3C-OC_2H_5$, was made by boiling triphenylchlormethane with absolute alcohol. The product was recrystallized once from alcohol and twice from petroleum ether. The substance was thus obtained in pure white crystals, melting sharply at 83° C. To 2 grams of this ethoxy compound was added an amount of freshly distilled acetyl chloride just sufficient for solution, and the mixture was boiled for about an hour. Upon cooling slowly, large white crystals, 1.5 grams, separated. After recrystallization, the product gave a melting-point of 112° C., and was identified by its properties and by analysis as pure triphenylchlormethane.

(2) Two grams of the ethoxy compound were dissolved in cold acetyl chloride. A small amount of heat was generated by the reaction, and crystallization commenced at once. A little petroleum ether was added and the mixture cooled in ice. The crystals, 1.8 grams, were washed with petroleum ether, recrystallized and analyzed. They melted at 111° C., and consisted of pure triphenylchlormethane. An analysis gave 12.91 per cent. chlorine; calculated, 12.75 per cent.

(3) The triphenylcarbinol, instead of the ethoxy compound, was next tried. Two grams were dissolved in acetyl chloride. The solution was of a violet color and changed to a dark red as the reaction progressed. Some heat was evolved in this reaction also. The crystals which separated on cooling, 1.7 grams, showed, on recrystallization, a melting-point of 109° C., and were found to consist of pure triphenylchlormethane. The analysis gave 12.67 per cent. chlorine.

The action of acetyl chloride upon triphenylcarbinol and upon its ethoxy compound is, therefore, as follows:

$$(C_6H_5)_3C-O-C_2H_5 + CH_3CO.Cl = (C_6H_5)_3C-Cl + CH_3COOC_2H_5.$$

$$(C_6H_5)_3C-O-H + CH_3CO.Cl = (C_6H_5)_3C-Cl + CH_3COOH.$$

Action of Acetic Anhydride.—(1) One gram of the pure carbinol was boiled for an hour with pure acetic anhydride. The acid was then distilled off under diminished pressure and the residue recrystallized from petroleum ether. The product, 0.9 gram, melted at 160° C., and was found to consist of unchanged carbinol.

(2) Another sample of triphenylcarbinol was boiled with acetic anhydride and anhydrous sodium acetate. The solution was filtered hot and concentrated, as before, under diminished pressure. The resulting product, which melted at 159° C., was again unchanged carbinol.

Herzig and Wengraf obtained, on boiling the reaction product from acetic anhydride and the carbinol with alcohol, triphenylcarbinol ethyl ether. But, as they themselves observe, this cannot be taken as a conclusive proof that the acetyl compound was the cause of its formation, because the carbinol itself gives, on boiling with alcohol in presence of a small amount of acetic acid, the ethyl ether compound. The experiments described above show that in reality no acetyl compound was formed.[1]

Triphenylmethyl Acetate.—We next prepared the acetyl compound by an indirect method,—by the action of silver acetate upon triphenylchlormethane. Four grams of triphenylchlormethane were dissolved in benzene, mixed with an excess of silver acetate and boiled, with reflux condenser, for two hours, moisture being carefully excluded. The solution was filtered hot and the excess of benzene distilled off. The crystals, which separated out on cooling with ice, were washed with petroleum ether and then recrystallized, twice from petroleum ether and twice from acetic ether. The melting-point of the crystals remained constant at 87°-88° C. The analysis gave:

	Calculated for $(C_6H_5)_3CO_2.CCH_3$.	Found. I.	Found. II.
Carbon	83.44	82.98	83.37
Hydrogen	6.01	6.06	5.99

The acetyl group was determined in the usual manner, by boiling the substance with an alcoholic solution of potassium hydroxide and titrating the excess of the alkali with a standard solution of acid. Calculated for $(C_6H_5)_3CO.OCCH_3$, acetyl, 15.25 per cent.; found, 13.19 and 13.07 per cent.

We have also prepared the acetyl compound without the employment of heat. One sample of triphenylchlormethane was suspended in absolute ether, an excess of silver acetate added, and the whole shaken for three weeks at the temperature of 25° C. A second sample, dissolved in benzene, was treated in the same way. In both instances, almost quantitative yields of very pure

[1] Compare Bistrzycki und Herbst: *Ber. d. chem. Ges.*, **35**, 3133 (1902).

triphenylmethyl acetate were obtained. The acetyl compound melts, as stated, at 87°-88° C. It is very soluble in the usual organic solvents, and, like so many other triphenylmethyl derivatives, shows a tendecy to separate from concentrated solutions in the form of an oil, which, on scratching, changes to a crystalline mass. Acetic ether gives the best appearing crystals. The compound is readily decomposed by water and by alcohol.

Action of Acetic Acid upon the Acetyl Compound.—It was found by one of us[1] that triphenylchlormethane reacts but slowly with cold glacial acetic acid, but quite appreciably when the solution is heated. It was also found[2] that hydrochloric acid acts upon triphenylcarbinol in acetic acid even when the latter contains as much as 10 per cent. water, and gives triphenylchlormethane. It was suggested that while in a 90 per cent. acetic acid solution the reaction is a reversible one in regard to carbinol (I), in absence of water it is similarly so in regard to the acetyl compound (II).

$$(C_6H_5)_3C.Cl + H_2O \rightleftarrows (C_6H_5)_3C.OH + HCl \qquad (I)$$

$$(C_6H_5)_3C.Cl + CH_3COOH \rightleftarrows (C_6H_5)_3CO.COCH_3 + HCl \qquad (II)$$

Experiment, however, shows that this is not the case in (II). Two grams of triphenylchlormethane were heated with a large excess of carefully purified glacial acetic acid on the water-bath, and a constant stream of dry carbon dioxide was passed through the solution for twenty hours. A careful examination of the residue, obtained on removing the acetic acid under diminished pressure, showed that, in addition to some triphenylchlormethane, it contained triphenylcarbinol, but none of the acetyl compound.

Action of Acetyl Chloride upon the Acetyl Compound.—The acetyl chloride for this experiment was carefully fractionated. A stream of thoroughly dried carbon dioxide was then passed through the chloride in order to free it completely from any hydrochloric acid gas which it might have contained in solution. One-half gram of pure triphenylmethyl acetate was gently warmed with the acetyl chloride. The excess of the liquid was removed in a stream of dry air, and the crystalline residue was dried in a vacuum dessicator over soda-lime. It melted at 109° C., and proved to be pure triphenylchlormethane. The analysis gave 12.97 per cent. chlorine; calculated, 12.75 per cent.

[1] *Ber. d. chem. Ges.*, **36**, 379 (1903).
[2] *Ibid.*, **36**, 384 (1903).

As Hemilian, Allen and Kölliker, and Herzig and Wengraf have all used acetyl chloride in the preparation of the substance described by them as triphenylmethyl acetate, and as the latter is decomposed by that reagent, it follows that the substance de-described by them as triphenylmethyl acetate, and as the latter It was, we believe, triphenylchlormethane. The latter would give, on treatment with water or with alcohol, the same products as the acetyl compound: the carbinol or the ethoxy compound. In fact, this is true of all the salts of thiphenylmethyl: the halides, the sulphate, the picrate, etc., are readily hydrolyzed.

ANN ARBOR, MICH.,
September, 1903.

ON THE POSSIBLE EXISTENCE OF A CLASS OF BODIES ANALOGOUS TO TRIPHENYLMETHYL.

[PRELIMINARY NOTICE.]

BY M. GOMBERG.

Received October 12, 1903.

IN THE several papers which I have published on the subject of triphenylmethyl, some important features in regard to the behavior of that substance were brought out.

(1) The extreme unsaturation of the compound, as evidenced by the action of atmospheric oxygen and of iodine upon it.

(2) The unusual property possessed by that unsaturated hydrocarbon of entering into combination with different oxygen compounds, such as ethers, esters, etc. It appeared probable that these combinations represent compounds wherein the oxygen acts as being tetravalent. It might be added here that triphenylmethyl unites with equal readiness with nitriles.

(3) Triphenylmethyl may be considered as a distinctly basic radical. This furnishes an explanation why triphenylchlormethane, also the bromide and the iodide, are *salts,* as judged by their purely chemical behavior, as well as by the physico-chemical tests; these halides, dissolved in liquid sulphur dioxide, are true electrolytes.[1] The same is true of the sulphate, as was found by Mr. L. H. Cone[2] in this laboratory. Even triphenyl-

[1] Gomberg: *Ber. d. chem. Ges.*, **35**, 2403 (1902); Walden: *Ibid.*, **35**, 2018 (1902).

[2] Mr. L. H. Cone, holder of a research assistantship to the Carnegie Institution, will publish his results in full later.

methyl itself possesses. in that solvent, a decided electrical conductivity, as has been recently shown by Walden.[1]

(4) Under the influence of catalyzing agents, such as dilute hydrochloric acid in benzene, ether, or some other solvent, triphenylmethyl is readily condensed to hexaphenylethane.[2]

It could hardly be expected that, whatever the constitution of triphenylmethyl, there should not be some other similar compounds capable of existence. The reaction which served for the preparation of triphenylmethyl was accordingly further studied, and an attempt has been made to apply it to compounds analogous to triphenylchlormethane. The following substances were subjected to this test:

Para-ditolylphenylchlormethane, $(CH_3.C_6H_4)_2(C_6H_5)C.Cl.$

Tritolylchlormethane, $(CH_3C_6H_4)_3C.Cl.$

Paratrinitrotriphenylchlormethane, $(NO_2.C_6H_4)_3C.Cl.$

Paratrimethoxytriphenylchlormethane, $(CH_3O.C_6H_4)_3C.Cl.$

In every case the initial stage of the reaction has been found to be the same as when triphenylchlormethane itself had been employed. A solution of the latter in benzene or in ether, when treated with zinc, silver, or mercury, assumes instantly a yellow color, which, as has been conclusively shown, is due to the formation of triphenylmethyl. Now, when any one of the four abovementioned derivatives of triphenylchlormethane is treated in the same manner, the reaction is strikingly similar to the one with triphenylchlormethane itself. The introduction of the metal into a solution of those substances is followed in every case by the instantaneous formation of a substance which imparts color to the solution. Moreover, just as the exposure to air in the case of triphenylmethyl brings about rapid oxidation of the hydrocarbon and the consequent decolorization of the yellow solution, so also in the case of the other four instances; exposure of the solutions to air destroys their color at once—due, no doubt, also to oxidation.

But while in the case of triphenylmethyl the oxidation is comparatively simple, and the resulting product, the peroxide, can be readily isolated, the oxidation by the atmospheric oxygen in the other instances is more complex. So far, I have succeeded in isolating the oxidation product pure enough for analysis only in one

[1] *Ztschr. phys. Chem.*, **43**, 443 (1903).

[2] *Ber d. chem. Ges.*, **35**, 3914 (1902); **36**, 376 (1903).

other instance, namely, in the case of the unsaturated hydrocarbon from tritolylchlormethane. Indeed, although there can be but little doubt that the action of metals upon the different triphenylchlormethane derivatives is probably the same in all instances, yet, in my experience, each case requires, for the successful course of the reaction, different experimental conditions. The nature of the metal, as well as the nature of the solvent, is of considerable influence upon the progress of the reaction. The subject becomes more difficult still because some of the chlor-compounds, as, for instance, the trinitrotriphenylchlormethane, are only slightly soluble in the usual organic solvents, which necessitates the use of large volumes of liquids.

The halides of triphenylchlormethane—the chloride, bromide, and iodide—are colorless in the solid state and also when dissolved in solvents which possess no ionizing power. But when dissolved in liquid sulphur dioxide, which does possess this power to a large extent, these halides dissociate into ions, $(C_6H_5)_3C^{\bullet}$ and Cl', as was proved by the electrical conductivity of the solutions. Moreover, such dissociation is invariably accompanied by the formation of a yellow color in the solvent. It was suggested[1] that the color was due to the ion $(C_6H_5)_2C^{\bullet}$. Since the free hydrocarbon, triphenylmethyl itself, while colorless in the solid state, on dissolving gives yellow solutions, it was inferred that the hydrocarbon exists in solution as ions $(C_6H_5)_3^{\bullet}$ and $(C_6H_5)_3C'$. The fact that triphenylmethyl, dissolved in liquid sulphur dioxide, shows very considerable electrical conductivity, argues, it seems to me, in favor of this view. There remains yet to account for the relation which exists between the two states of triphenylmethyl, the colorless solid and the yellow when in solution. If, however, it be true that the color of the solution of triphenylmethyl is really due to the latter existing in solution in the ionic state, then it must follow that a variation in complexity of the radical should also cause a variation in the color of the radical when the latter is in solution and hence in the ionic state. This is actually the case. Solutions of triphenylchlormethane acquire, on the addition of metals, a distinctly yellow color. The ditolylphenyl- and especially the tritolylchlormethane, when subjected to the similar treatment, give orange solutions with quite a perceptible tinge of red. Trinitro-

[1] Gomberg: *Ber. d. chem. Ges.*, **35**, 2406 (1902).

triphenylchlormethane, even in minute quantities, gives, on the addition of metals (silver), a beautiful greenish-blue solution which changes, on warming, first to a violet-red and finally to a genuine fuchsine-red. On cooling, the blue color is restored; on exposure to air the solution is at once decolorized.

I shall continue the study of this reaction and shall extend it to other derivatives of triphenylhalogenmethane.

ANN ARBOR, MICH.,
September, 1903.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

AN EFFICIENT ASBESTOS OR GRAPHITE MUFFLE.

BY J. M. PICKEL AND C. B. WILLIAMS.

Received October 15, 1903.

AT THAT point in the determination of potash in fertilizers, where ammonium salts and the excess of sulphuric acid are driven off, it was formerly the practice in this laboratory to accomplish the volatilization by placing the platinum dish on the top of the glass chimney of an Argand gas-burner, such as is commonly used for illuminating purposes. To afford air-vent and gas escape, the dish rested on small wires (of iron) bent over the edge of the chimney. A battery of ten or twelve of these burners was aligned on the same gas-pipe.

After excess of acid was evaporated and the ammonium salts more or less volatilized, the dishes were removed from the Argand burners to the blast-lamp, and there, at a red heat, the volatilization completed and the organic matter destroyed. In hope of obviating the necessity of transferring the dishes to the blast, one of us (Pickel) introduced, during the winter of 1900, the following modification:

The chimneys were cut down to a length of about 4 cm., and the dishes brought into close proximity with the flame. The dishes were, moreover, enclosed in asbestos cups, in the bottom of which were cut round holes of such diameter as to fit snugly over the chimneys which were thus made to support the cups. An asbestos lid, having a vent hole of about 2 cm. diameter, covers each cup. Each platinum dish rested on a pipe-stem triangle, or

other suitable support placed on the bottom of the cup. It was found that the dish, thus muffled, could, after excess of acid had been driven off by a low flame, be easily brought to a red heat by merely turning up the flame; all ammonium salts could be volatilized completely, and organic matter destroyed, thereby obviating the use of a blast-lamp, except in rare cases. As the intense heat generated in the muffle softened, and, after a few days, distorted the glass support, it was, therefore, dispensed with, and a small asbestos cylinder, having in its side a narrow slot, or small, round hole through which to see and regulate the flame, substituted.

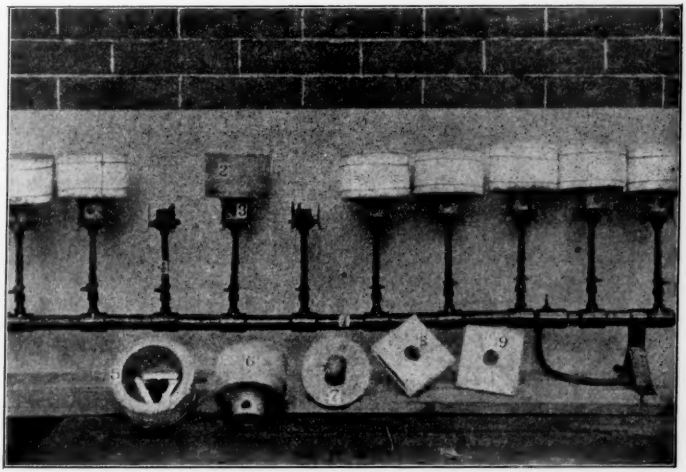
The material used in making this little muffle was asbestos board of about 0.6 cm. thickness. After cutting the board to proper shape and size, it was saturated with water, and, while wet, formed into a cylinder by rolling it around a tin can, or bottle, or other suitable core, and left till dry. The bottom was then fitted in and the whole held securely together by wires bound around near the top and bottom.

A battery of twelve of these little muffles was used throughout the greater part (two or three months) of a fertilizer season, and 500 or 600 potash determinations made with them. All incinerations of cotton-seed meal, cotton-seed hulls and tobacco stems were made in them, the usual larger and cumbersome muffles for that purpose being entirely dispensed with. Slightly changed in form, the muffles are, of course, equally suitable for use with a Bunsen burner. They were thus found efficient for roasting small assays of sulphurous gold ores, the finely powdered ore being contained in an ordinary evaporating dish.

Although the idea of these muffles—a separate muffle for each dish or crucible—grew out of the desire to facilitate the work of volatilization and incineration, it is not new. (The Erdmann furnace, which is figured and described in the chemical catalogues as a clay cylinder on a tripod over a Bunsen burner, involves the same idea.)

The efficiency and convenience of these little muffles for incinerations, ash determinations, roastings and volatilizations, and the ease with which any one can make them for himself, should create for them a place in the laboratory. But for daily use, year in and year out, they are not sufficiently durable when made

of asbestos, as above described. One of us (Williams) sought to remedy this defect, first, by constructing the muffles of metal (copper) and covering them inside and out with asbestos. But these, although in other respects satisfactory, were lacking in durability; the metal oxidized rapidly, and the asbestos needed renewal every few months. The material finally adopted (by him) was graphite, with a jacket of asbestos on the outside. This has proved altogether satisfactory. A battery of twelve of these graphite muffles, aligned on the same gas-supply pipe, and each heated by an Argand gas-burner, has now been in daily use for about two years in our laboratory, and has entirely superseded the usual form of muffle, for incinerations, ash determinations and the like. A point of special convenience with this piece of apparatus is that one or more, up to a dozen determinations may be made at one time, and that each is under separate control and regulation. The lids in use consist of an asbestos board, a plate of aluminum and a sheet of platinum riveted together; the asbestos forms the top of the lid and the platinum



the bottom, its object being cleanliness. But less-costly graphite covers answer quite as well. In the center of each lid is a vent-hole of about 3 cm. diameter. The muffles may be of any size. Ours have the following dimensions: The main body or re-

ceptacle, diameter (internal) and depth (internal), each 9.5 cm.; thickness of wall, 1 cm.; the small cylinder support, length, 3.5 cm.; diameter (adjusted to the size of burner in which it is to rest), in our case, 5.2 cm. outside, and 3.5 cm. inside.

These muffles may, of course, be used with any common Bunsen burner by placing them on a tripod.

The accompanying cut shows the parts of the battery of muffles: 1 is the gas-supply pipe, 2.5 cm. in diameter; 4 is a smaller pipe, provided with an air-hole and gas-cock, which feeds the Argand burner above; 2 shows the muffle in position and without asbestos covering; at 3 is a small hole through which the gas is lighted, and through which the flame may be seen and regulated; 5 gives an inside view of the muffle; 6 shows the under part of a muffle; 7 shows the top side of a graphite lid, the central vent-hole of which is hidden by its handle; and 8 and 9 are top and bottom views of the asbestos-aluminum-platinum lids.

REVIEW.

RECENT WORK IN INORGANIC CHEMISTRY.

By Jas. Lewis Howe.

Few notable papers have appeared during the past year on theoretical inorganic chemistry. Perhaps the most important is one by Abegg[1] on a new theory of valence. The author assumes the existence of two kinds of valence, with opposite polarity, in each atom. These he calls normal valence and contra-valence. The sum of the valences of an atom is eight. Thus chlorine has a negative normal valence of one and a positive contra-valence of seven. Negative contra-valences are much weaker than positive, since positive electrons are much more firmly attached to matter than the negative. The inert gases have a normal valence of zero and an (unexercised) contra-valence of eight. In his paper, Abegg applies these conceptions to the so-called molecular compounds.

In two papers,[2] Werner has developed his theory of primary and secondary valences with reference to the constitution of the ammonium and the oxonium compounds. Locke[3] has again attacked the theory of electro-affinity of Abegg and Bodländer, and holds that while the electro-affinity of the elements bears a close and interesting relation to the properties of many salts, it does not furnish a rational principle for chemical classification.

Erdmann claims[4] that the distinction enunciated by him in

[1] *Vid. Skrift.* I, 1902, No. 12.
[2] *Ann. Chem.* (Liebig), **322**, 261, 296.
[3] *Am. Chem. J.*, **28**, 403.
[4] *Zischr. anorg. Chem.*, **32**, 404.

1892, between metals and non-metals, *viz.*, that metals are those elements whose molecules consist of single atoms, while non-metals are those whose molecules contain several atoms, has been confirmed by all the more recent work along this line. On the other hand, Martin,[1] reasoning from the fact that in the same group the metallic characteristics of an element increase with the atomic weight and that among the non-metals the metallic character increases with the temperature, draws the conclusion that the metallic and non-metallic conditions are merely phases which each element can assume. At higher temperatures non-metals become metallic, their electrical conductivity increasing rapidly; in the vicinity of absolute zero, metals become non-conducting metalloids.

In the consideration of the periodic table, Brauner[2] suggests that the difficulty of accounting for the place of the rare earths will be minimized if we put them as a group in the place usually assigned to cerium. Thus, in this place we shall have *Ce, etc., 140-178*, followed immediately in the next space by *Ta 184*. In this way the vacant ninth period of Mendeléeff's table disappears. Brauner begins his table with Group 0, which is made up of the inert gases.

The study of double salts continues to attract increasing attention, though no satisfactory theory of their constitution has yet appeared. An important contribution to the chemistry of the double halides is the *Habilitationsschrift* of P. Pfeiffer.[3] Following up the systematic treatment of the double chlorides by Werner, he takes up the bromides and iodides from the same standpoint, and after a theoretical discussion of these salts, he gives a systematic survey of the whole field, with references to the literature. In connection with his study of vanadium salts, in which many new double halide compounds have been prepared, Ephraim[4] discusses these salts from a theoretical standpoint, holding that their constitution is largely dependent upon the atomic volume of the constituent elements. In particular, he formulates the law that the number of halogen alkali molecules which can unite to the halide of the heavy metal acting as a central nucleus, decreases with the increasing atomic weight of the positive metal. Grossmann[5] denies that the facts accord with this law. In a number of cases, such as $PbBr_2,4CsBr$, the highest value is reached with the cesium salt. Rubidium and ammonium salts often show a strong analogy which may be conditioned by the fact that they possess a similar atomic volume. Nor do the double cyanides, which are, according to Werner, of the same character as the halides, follow Ephraim's law. Grossmann's conclusion is that

[1] *Chem. News*, **86**, 295.

[2] *Ztschr. anorg. Chem.*, **32**, 1.

[3] Partially republished in *Ztschr. anorg. Chem.*, **31**, 191.

[4] *Ber. d. chem. Ges.*, **36**, 1177.

[5] *Ibid.*, **36**, 1600.

no comprehensive rule can be, at present, laid down regarding the composition of double salts. The discussion is being continued by Ephraim,[1] who has also prepared a series of new antimony double salts, and by Grossmann,[2] while Pfeiffer[3] and Jordis[4] both fail to find an experimental foundation for Ephraim's law. The probability is that there is a considerable sub-stratum of truth in the so-called law, but that it represents only a part of the truth. At all events, it is encouraging to find an increasing number of keen minds attacking this important problem of the double salts. Mention should be made, in this connection, of the interesting class of triple thiocyanates under investigation by Wells,[5] and the double periodates and manganese studied in the same laboratory by Price.[6]

In an address before the Fifth International Congress of Applied Chemistry at Berlin, Moissan gave a review of his work on the metallic hydrides. The alkali and alkali-earth hydrides are definite crystalline compounds and have nothing of the nature of hydrogen alloys. They are strong reducing agents, decomposing water with the evolution of hydrogen, forming formates with carbon dioxide and hydrosulphites with sulphur dioxide. With acetylene they form double compounds, of which K_2C_2,H_2C_2 is a type; on heating the latter, acetylene is evolved and the metallic carbide left.

A new preparation of nitrides has been discovered by Guntz.[7] When lithium nitride acts upon metallic chlorides, much heat is evolved and the corresponding nitride formed. This appears to be a method of general application. Lithium hydride seems to give a similar reaction, but it is so violent that it has not yet been possible to isolate the hydride, which is formed.

Moissan continues to enlarge our knowledge of the silicides. While it has been found very difficult to prepare the potassium and sodium silicides corresponding to silicon-ethane, Si_2H_6, the lithium compound, Li_6Si_2, is prepared by direct union of the elements in a vacuum. It is naturally a very active substance, decomposing water and acids generally with evolution of hydrogen, but when very concentrated hydrochloric acid is used the silicon-ethane is obtained, which is collected as a liquid by the use of liquid air.[8] Moissan has also prepared two silicides of vanadium, V_2Si and VSi_2. Lebeau has studied the silicides of cobalt, manganese and chromium. In the case of the last two metals, he has investigated, from a physical standpoint, the equi-

[1] *Ber. d. chem. Ges.*, **36**, 1815, 1912.
[2] *Ibid.*, **36**, 2499.
[3] *Ibid.*, **36**, 2519.
[4] *Ibid.*, **36**, 2539.
[5] *Am. Chem. J.*, **28**, 245; **29**, 474; **30**, 184.
[6] *Ibid.*, **30**, 182.
[7] *Compt. Rend.*, **135**, 738.
[8] *Ibid.*, **134**, 1083, 1549; **135**, 1284.

librium which exists between copper, silicon and manganese, and copper, silicon and chromium. This has enabled him to prepare several new silicides.[1]

Muthmann and Kraft[2] have prepared the hydrides and nitrides of cerium and lanthanum by burning the metals in hydrogen or nitrogen. In hydrogen, cerium ignites at 250°, while in pure oxygen its kindling temperature is little above 150°. In nitrogen, cerium does not ignite until 850° is reached. The kindling temperature of lanthanum is, in each case, somewhat higher than that of cerium. The hydrides and nitrides of these metals are stable in dry air, but are quickly decomposed by water or in the presence of moisture.

Several articles have appeared from the laboratory at Odessa, continuing the work of Pissarjewski on the compounds of inorganic salts and acids with hydrogen peroxide. The carbonates, arsenates, tungstates, uranates, vanadates, and the rare earths are included in this list. There is a very decided question as to whether many of these compounds are to be considered as true peroxides, or whether some of them, which have been designated as pseudo-peroxides, should not rather be considered as compounds in which the hydrogen peroxide is present in the form of a so-called peroxide of crystallization. This is discussed by Tanatar in a recent paper,[3] and by Willstätter.[4] A new class of peruranates has also been described by Alloy,[5] having the formula M_2UO_8. In a lecture at the meeting of the Verein of the German chemists at Düsseldorff, Staedel illustrated the preparation of pure hydrogen peroxide. A 95 per cent. solution was solidified by the ether-carbon dioxide mixture. When, to a new portion of the 95 per cent. solution, at a temperature of —10°, a little of the solid is added, crystals of pure hydrogen peroxide begin to form. On recrystallization, these consist of 100 per cent. hydrogen peroxide, and this is suggested as the safest method of preparing the anhydrous compound. The crystals are fairly stable, but are exploded at once by contact with platinum black or pyrolusite. With the monohydrate of sulphuric acid, ozone is at once formed. Some interesting notes on ozone are contributed to the *Berichte* (**35**, 2902) by Arnold and Mentzel. Tetramethyl-*p*-*p*′-diaminodiphenylmethane (tetra-base for short) is proposed as the best reagent for gaseous ozone, to differentiate it in the presence of other gases which have action upon starch-iodide paper. Ursol D, which had been suggested by Chlopin for a similar purpose, is shown to be useless, as its supposed characteristic reaction is caused by the impurities present and not by ozone.

[1] *Compt. Rend.*, **136**, 231, 1329.
[2] *Ann. Chem.* (Liebig), **325**, 261.
[3] *Ber. d. chem. Ges.*, **36**, 1893.
[4] *Ibid.*, **36**, 1828.
[5] *Bull. Soc. Chim.* (3), **29**, 292.

Dudley[1] has studied the action of sodium peroxide on several more metals. With nickel, $Ni_3O_4,2H_2O$ is formed, which loses water at 240°. It is unlike Daubigny's Ni_3O_4 in its properties. Iron gives Fe_3O_4,H_2O in tabular, magnetic crystals. Gold is rapidly attacked, but the oxide formed is immediately decomposed, giving spongy gold. Silver is also rapidly acted upon with the formation of gray crystals, which seem to be a lower oxide. Spongy platinum burns with the peroxide like tinder, giving, after washing, $Pt_2O_3,2H_2O$. On heating, the sesquioxide is left, which is a new oxide of platinum.

Moissan has continued his studies on fluorine, examining, in conjunction with Dewar, the action of the element at low temperatures.[2] The melting-point of solid fluorine was found to be — 223°. The solid fluorine reacted with liquid hydrogen at — 252.5° (20.5° absolute) with explosive violence. At — 187°, the reactions of various compounds and elements with liquid fluorine are hardly less violent than at higher temperatures, its affinity being little in abeyance even at this low temperature. Iodine pentafluoride has been prepared by Moissan[3] and proves to be so stable that it can be distilled in hydrogen without decomposition.

Starting from the fact that chlorine is liberated from hydrochloric acid by Caro's reagent, Wedekind[4] has attempted the use of the analogous reaction for the preparation of fluorine. Caro's reagent, however, had no action upon hydrofluoric acid, neither fluorine being evolved directly, nor any trace of ozone, which might indicate that it had been temporarily formed.

By using a modification of the Goldschmidt process, the magnesium, aluminum, and oxides being taken in such proportions as to give the composition of the natural matrix of the diamond, von Hasslinger[5] has succeeded in converting finely divided graphite into clear, octahedral diamonds of 0.5 mm. diameter. The interesting point about this synthesis is that the diamonds are formed by slow cooling in the absence of any considerable pressure.

A new variety of phosphorus has been prepared by Schenck,[6] by heating white phosphorus to boiling in PBr_3 for ten hours. It is light red, resembling, in appearance, the ordinary red modification, and, like it, being physiologically inert, but, on the other hand, it is very active chemically, often more so than white phosphorus.

For the preparation of phosphine, Bodroux[7] uses a crude aluminum or magnesium phosphide, made by igniting a mixture

[1] *Am. Chem. J.*, **28**, 59.
[2] *Compt. Rend.*, **136**, 641, 785.
[3] *Ibid.*, **135**, 563.
[4] *Ber. d. chem. Ges.*, **35**, 2267.
[5] *Monatsh. Chem.*, **23**, 817.
[6] *Ber. d. chem. Ges.*, **36**, 979.
[7] *Bull. Soc. Chim* (3), **27**, 568.

of 2 parts aluminum (or magnesium) and 1 part red phosphorus. The resulting mass gives off pure phosphine slowly on treatment with cold water, and more rapidly when the water is warm. Above 50° the phosphine is contaminated with hydrogen, as is the case when acids are used.

Stock and Hoffmann,[1] by the action of ammonia on phosphorus pentasulphide, have prepared a series of amino- and imino-thiophosphoric acids, and by the successive elimination of ammonia and hydrogen sulphide obtain at last phosphorus nitride, P_3N_5. This interesting compound proves to be a white, insoluble, odorless and tasteless body, stable up to a low red heat. Although outside of the strict range of inorganic chemistry, it should be noted here that Michaelis and his pupils have developed much further the organic compounds containing both phosphorus and nitrogen, forming several hundred compounds.[2]

The metaphosphates have been subjected to a somewhat extended investigation by Warschauer,[3] who finds that Fleitmann's dimetaphosphate is in reality a tetrametaphosphate. This result is confirmed both by the Ostwald-Walden valence law, and by the transference number of the sodium salt. When lead oxide is heated with phosphoric acid, if the temperature is kept below 400°, the tetrametaphosphate is formed, while above that temperature a different modification, Fleitmann's 'tetrametaphosphate,' appears, which is, in all probability, the hexametaphosphate. He also finds that the solutions of the hexametaphosphate decompose directly into the orthophosphate, but a small amount of the pyrophosphate is formed at the same time.

Erdmann and Unruh[4] have made a study of the yellow modification of arsenic, first described by Linck in 1899. It is prepared by the rapid cooling of arsenic vapor, and must be immediately dissolved in carbon bisulphide or benzene to prevent its almost instant conversion into the ordinary metallic arsenic. Erdmann prepared a large quantity by collecting the vapor directly in carbon bisulphide. It may be obtained in solid form by cooling a saturated solution to — 70°, but is exceedingly unstable. By the gradual action of light on the solution, a new red-brown modification of arsenic is obtained. The molecular weight of the yellow modification corresponds to the molecule As_4. From the fact that vitreous arsenious oxide is formed by rapid cooling, Erdmann concludes that it contains a ring of four arsenic atoms, and he has succeeded in obtaining a small quantity of yellow arsenic by the reduction of this form of the oxide.

[1] *Ber. d. chem. Ges.*, **36**, 314.
[2] *Ann. Chem.* (Liebig), **326**, 129, 171, 220.
[3] *Ztschr. anorg. Chem.*, **36**, 137.
[4] *Ibid.*, **32**, 437.

The pentachloride of arsenic has been obtained by Baskerville and Bennett[1] by the action of chlorine on the trichloride at very low temperatures.

Our knowledge of the halide double salts of quinquivalent antimony has been very materially enlarged by Weinland and Feige,[2] who have prepared a series of double chloro- and bromo-antimonates. Most of these are derived from metachloro-antimonic acid, $HSbCl_6$, and the corresponding bromo-acid. A second salt of quadrivalent antimony, Rb_2SbBr_6, was also found.

After a study of sundry alloys of antimony, Stock and Doht[3] find that the alloy of antimony with 2 parts magnesium is best suited for the preparation of stibine. This alloy is treated with hydrochloric acid, the gas is carefully dried and condensed by the use of liquid air. The fusing-point of stibine is —88°, its boiling-point —17°. When pure, it is fairly stable for a few hours, but is immediately decomposed at 150°.

By an examination of the composition of the vapor of a mixture of S_2Cl_2 and chlorine, Ruff[4] finds that the supposed compound SCl_2 has no existence. The same is true of SBr_2 and SBr_4,[5] while Boulouch[6] has, by the use of the dilatometer, proved that none of the supposed compounds of sulphur and iodine have any claim to recognition. Russel and Smith[7] have failed to find any evidence for the existence of Deninger's carbon monosulphide, but Thomsen later shows that it is really formed by the action of hot copper upon a mixture of carbon bisulphide and nitrogen, but it has not proved possible to isolate it.[8]

Contrary to the views of Ringer and Muthmann, that the supposed compounds of sulphur and selenium are isomorphous mixtures of the elements, Rathke[9] considers that in this mixture there are present not less than two distinct compounds of sulphur and selenium. He suggests that it is possible that in the sulphur molecule, S_8, a larger or smaller number of the sulphur atoms may be replaced by selenium. Rathke also considers that the characteristic decayed horseradish odor, when selenium is heated on charcoal, is due to carbon selenide, which, even in the most extreme dilution, has the same odor.

In his *Habilitationsschrift* (Breslau, 1903), Meyer shows that P_4Se_3 and P_2Se_5 are to be looked upon as distinct chemical compounds, but that P_4Se and P_2Se do not exist.

[1] This Journal, **24**, 1070.
[2] *Ber. d. chem. Ges.*, **36**, 244.
[3] *Ibid.*, **35**, 2207.
[4] *Ibid.*, **36**, 418.
[5] *Ibid.*, **36**, 2437.
[6] *Compt. Rend.*, **136**, 1551.
[7] *Proc. Chem. Soc.*, **18**, 197.
[8] *Zischr. anorg. Chem.*, **34**, 187.
[9] *Ber. d. chem. Ges.*, **36**, 594.

Several interesting classes of double salts of selenates with iodates, phosphates and arsenates have been prepared by Weinland and Barttlingck.[1] The complex iodates are of the formulas

$$I_2O_5,2SeO_3,2R_2O,H_2O$$

and

$$3I_2O_5,2SeO_3,2R_2O,5H_2O;$$

the phosphates and arsenates follow the types

$$P_2O_5(As_2O_5),2SeO_3,2R_2O,3H_2O$$

and

$$P_2O_5(As_2O_5),5SeO_3,3.5K_2O,5.5H_2O.$$

All these salts crystallize well.

Some considerable work has been done along the line of improvements in the electrolytic preparation of calcium. Borchers and Stockem[2] use fused calcium chloride as the electrolyte, starting the current through a thin carbon rod. Their calcium is spongy, but may be pretty thoroughly freed from calcium chloride by squeezing when fused. They prepare strontium by the same method, and find it is as soft as lead. Arndt[3] modifies this method by using the electric arc, and obtains a calcium 99 per cent. pure. Ruff and Plato[4] discuss the subject very fully, and describe their process for producing the metal, either on a small or on a large scale. The most important point in their process is the use of a mixture of calcium salts as an electrolyte. The best mixture they find to be about 1 part of fluor-spar to 6 of calcium chloride. Their calcium is pure white, somewhat harder than lead.

Goodwin and Smith[5] describe an apparatus for the preparation of calcium by the electrolysis of calcium chloride.

The difficulties attending the electrolytic preparation of barium are shown by Guntz[6] to be due to the formation of a 'basic' chloride, BaCl, which he has prepared in a pure state. This chloride forms double salts with the alkali chlorides, which are also formed when barium chloride is heated with metallic sodium or potassium.

Attention is called by Granger[7] to the fact that at 600° aluminum becomes granular and exceedingly brittle. At a somewhat higher temperature it is very soft as well as granular, and is easily pulverized in small quantities. In the *Comptes Rendus* (135, 791), Verneuil discusses, at some length, the conditions necessary for the production of artificial rubies. It appears, among other conditions, that the temperature must be but little above the point of fusion of alumina, else the melted mass will

[1] *Ber. d. chem. Ges.*, **36**, 1397.
[2] *Ztschr. Elektrochem.*, **8**, 757.
[3] *Ibid.*, **8**, 861.
[4] *Ber. d. chem. Ges.*, **35**, 3612.
[5] This Journal, **25**, 873.
[6] *Compt. Rend.*, **136**, 749; *Bull. Soc. Chim.* (3), **29**, 490.
[7] *Bull. Soc. Chim.* (3), **27**, 789.

become opaque on cooling. In less than two hours, Verneuil prepared a ruby of nearly 3 grams weight, which could not be distinguished from the natural stone. The utmost accuracy in conforming to the necessary conditions is demanded to attain such a result.

During the past year a considerable amount of work has been done upon thallium. Especially has there been an effort to obtain thallium alums, in which thallium is the trivalent metal. Numbers of double sulphates have been obtained by Marshall,[1] and Meyer and Goldschmidt,[2] but in no case an alum. The nearest approach to a solution of the problem is by Piccini and Fortini,[3] who have prepared mixed crystals of ammonium alum in which a portion of the aluminum is replaced by thallium. They have not succeeded, however, in preparing the pure thallium alum. The thallium oxalates have also interested Meyer and Goldschmidt,[4] as well as Rabe and Steinmetz,[5] particularly in the effort to form complex thallium salts. While their efforts in this direction were not attended with success, numerous new, double oxalates were discovered. Meyer and Goldschmidt also prepared double salts of thallic acetate and of thallic nitrate, both rather rare classes of salts.

Investigations upon the rare earths have not been neglected during the past year, though few new ideas have been brought out. Drossbach[6] splits didymium into its components by the use of a concentrated potash solution, and the recrystallization of the double magnesium nitrate. From a potash solution containing cerium, lanthanum and didymium, he precipitates pure cerium quantitatively by a current of chlorine. Meyer and Koss[7] have studied the iodimetry of cerium dioxide and the didymium oxides, perfecting a method for the estimation of the former. Following up his work upon the preparation of the anhydrous chlorides of neo- and praseodymium, Martignon[8] has studied the effect of heat upon the chlorides of samarium, yttrium and ytterbium in a current of dry hydrogen chloride. $SmCl_3,6H_2O$ loses 5 molecules of water at 110° and the last at 150°. Anhydrous samarium chloride is a yellow powder darkening with heat and fusing to a dark brown liquid at about 1000°, but regaining its original color on cooling. It is very deliquescent and evolves much heat on solution in water. The anhydrous chlorides of yttrium and ytterbium are very similar to that of samarium.

[1] *Proc. Roy. Soc.* (Edin.) **24**, iii, 305.
[2] *Ber. d. chem Ges.*, **36**, 238.
[3] *Ztschr. anorg. Chem.*, **31**, 451.
[4] *Loc. cit.*
[5] *Ber. d. chem. Ges.*, **35**, 4447.
[6] *Ibid.*, **35**, 2826.
[7] *Ibid.*, **35**, 3740.
[8] *Compt. Rend.*, **134**, 1308.

Starting with a mixture of the yellow oxides obtained in the preparation of didymium from monazite by the chromic acid method and fractioning with ammonia and then with oxalic acid, Marc,[1] while failing to isolate terbia, has thrown light upon the subject. He concludes that the so-called terbia is a mixture of yttria and another heavier earth, probably ytterbia, colored with a small amount of the real terbia. Terbium has two oxides, the lower white and the higher colored. It probably has an absorption spectrum in which the principal band is $\lambda = 464\text{-}461$. Its atomic weight should be about 157. Cleve's thulia he considers to be an yttria-ytterbia mixture with a little holmia and terbia, and Cleve's decipia a gadolina-yttria mixture colored with praseodymia. Cleve has separated out a very pure ytterbia and described a long list of its salts.[2] Ytterbium is always trivalent and resembles most closely yttrium and erbium. Rosenheim[3] has described a large number of new thorium salts, some of them with organic acids. He also finds thorium chloride to form compounds with many organic oxygen compounds such as alcohol, aldehyde, acetone, and benzaldehyde.

According to Elba, by the electrolysis of hydrochloric acid with a lead anode $PbCl_2$ is formed, but with two anodes, one of lead and one of carbon, the $PbCl_2$ formed is oxidized by the chlorine at the carbon anode to $PbCl_4$. The double chloroplumbates can be prepared in this way, and the slightly soluble quinoline salt can be used to determine the production of the tetrachloride quantitatively.[4] Seyewetz and Trawitz[5] prepare the ammonium chloroplumbate by adding a moist lead dioxide in small portions to an excess of concentrated hydrochloric acid at 0°, and also[6] by the action of ammonium persulphate on lead dichloride. The chloroplumbate is used by them as a very effective agent for chlorination in organic chemistry.

Titanium trichloride and other compounds of trivalent titanium have been found by Knecht[7] to be excellent reducing agents, far more powerful than stannous chloride. Among other instances, nitro compounds are instantly reduced to amines.

By electrolytic reduction Piccini and Marino[8] have prepared a number of salts of bivalent vanadium. The sulphates belong to the ferrous-iron type, crystallizing alone with 7 molecules of water, and as alkali double salts with 6 molecules. Isomorphous, crystal mixtures were formed of vanadium-magnesium, and of vanadium-ferrous sulphates. Quadrivalent vanadium is being

[1] *Ber. d. chem. Ges.*, **35**, 2382.
[2] *Ztschr. anorg. Chem.*, **32**, 129.
[3] *Ibid.*, **35**, 424.
[4] *Ztschr. Elektrochem.*, **8**, 512.
[5] *Bull. Soc. Chim.* (3), **20**, 455.
[6] *Compt. Rend.*, **136**, 686.
[7] *Ber. d. chem. Ges.*, **36**, 166.
[8] *Ztschr. anorg. Chem.*, **32**, 55.

investigated by Koppel and Behrendt.[1] In their first communication they described a series of simple and double vanadyl sulphates, and another of sulphites.

An extended investigation of chromium salts has been begun by Wyrouboff,[2] with especial reference to the constitution of the violet and green modifications. He considers that the violet salts always contain the group $Cr_2(OH)_6$, to which the acid is added. Thus the hydrated violet sulphate has the formula

$$Cr_2(OH)_6,3H_2SO_4,10H_2O,$$

while the anhydrous form is

$$Cr_2(OH)_6,3H_2SO_4.$$

On the other hand, the green salts contain the radical

$$Cr_2(OH)_2(OH)_4,$$

in which two hydroxyls are acid and four basic. Thus we have the green salts

$$Cr_2(OH)_2(OH)_4,2H_2SO_4$$

and

$$Cr_2(OH)_2,2KOH,(OH)_4.$$

The formation from the violet salt is not merely a loss of water, but often a loss of acid. The chromosulphuric acids exist in several modifications, the first member of the series having the formula

$$[Cr_2O(OH)_2(OH)_2(SO_2)_4]O(OH)_4(OH)_2,$$

the last two hydroxyls being acid in their nature. Wyrouboff holds that many of the seemingly simple inorganic compounds are in reality very complex and must be likened in their constitution to the compounds of organic chemistry. By the action of hot concentrated hydrochloric acid, Recoura[3] finds that chromium sulphate is converted into a chlorosulphate,

$$CrSO_4Cl,6H_2O,$$

in which the chlorine is not immediately precipitable by silver nitrate, while the sulphate group is immediately precipitated by barium chloride. On heating this compound to 85°, it gradually loses 1 molecule of water, the sulphate group is no longer affected by the barium chloride, and its aqueous solution is a non-electrolyte. Aluminum forms a similar chlorosulphate, but iron does not.

The question of the existence of bichromates of any metals except those of the alkalies has been settled by Autenrieth,[4] who prepares silver bichromate, $Ag_2Cr_2O_7$, by double decomposition in the presence of nitric acid, and also by the action of silver nitrate on chromium trioxide. Barium bichromate was also obtained, but not lead bichromate. He further clears up the reac-

[1] *Ztschr.. anorg. Chem.*, **35**, 154.
[2] *Bull. Soc. Chim.* (3), **27**, 666, 719.
[3] *Compt. Rend.*, **135**, 163.
[4] *Ber. d. chem. Ges.*, **35**, 2057.

tion for the preparation of chromyl chloride, by finding that while a 20 per cent. hydrochloric acid gives, with chromium trioxide, only chlorine, if the acid is 35 per cent. to 40 per cent. strong, a large amount of the chromyl chloride is obtained. A double chromate has been at last prepared by Briggs,[1] who, by the action of ammonium chromate on nickel sulphate, has obtained the ammonium nickel sulphate

$$(NH_4)_2Ni(SO_4)_2,6H_2O.$$

The pure potassium salt was not made, but an isomorphous mixture of the potassium-nickel sulphate and chromate was obtained.

Doering[2] has made an extended study of a chromium, 97 per cent. to 98 per cent. pure, prepared by the Goldschmidt process. The metal is rapidly dissolved by hydrochloric acid, $CrCl_2$ being first formed, but the whole being eventually converted into $CrCl_3$. Since in a hydrogen atmosphere the bichloride is rapidly converted into the trichloride only in the presence of catalytic agents, such must be present in this solution of chromium. This agent was found to be Geuther's oxide of silicon, $Si_3H_2O_5$, formed from the silicon present as an impurity in the chromium. The fusing-point of a similar chromium, 99 per cent. pure, was found by Lewis[3] to be 1515°.

Several pieces of valuable work on tungstates have been carried out in the laboratory of the University of Pennsylvania under the direction of Dr. Edgar F. Smith, and published in this Journal.[4] The so-called para- and metatungstates have been investigated by Taylor, who finds all the known ammonium salts to have a complex formula. He assumes that in all these salts the group $2NH_4OH,4WO_3$ is present as a nucleus, the side chains containing varying proportions of NH_4OH,WO_3 and H_2O. A new class of complex tungstates, containing vanadium and phosphorus, or arsenic, in different stages of oxidation, has been described by Smith and Exner, and further developed by Rogers.

$$13(NH_4)_2O,2P_2O_5,8V_2O_5,34WO_3,86H_2O$$

may be cited as an example of one of these salts. Friedheim and Henderson[5] have described a somewhat similar class of tungstates containing vanadic and silicic acids.

Interest in the subject of colloids has greatly increased among chemists since Bredig's work upon colloidal platinum and several new methods of preparing metallic and other colloids have been recently described. By means of hydrazine hydrate, hydroxylamine hydrochloride, or hypophosphorous acid, Gutbier[6] obtains hydrosols of gold, silver, platinum, mercury, and copper, as well

[1] *J. Chem. Soc.*, **83**, 401.
[2] *J. prakt. Chem.* (2), **66**, 65.
[3] *Chem. News*, **86**, 13.
[4] This Journal, **24**, 573, 629; **25**, 298.
[5] *Ber. d chem. Ges.*, **35**, 3242.
[6] *Ztschr. anorg. Chem.*, **31**, 448; **32**, 292, 347.

as of selenium and tellurium. The gold hydrosol prepared by the action of hydrazine on a dilute neutral solution of gold chloride, is blue and resembles that obtained by Bredig electrolytically. It is very stable in the cold, but on warming is immediately converted into the hydrogel. Gutbier also obtains hydrosols of tellurium disulphide and trisulphide, and of selenium disulphide. Kuespert uses formaldehyde as his reducing agent[1] in the presence of water-glass. He prepares a hydrosol of copper acetylide by adding a trace of copper and ammonia to water, which has been shaken up with acetylene. Henrich's reducing agents[2] are the photographic developers, of which he finds pyrogallol the best for the production of colloidal metals. By varying his solvents, he gets organosols of gold with ether, acetone, and alcohol. He calls attention to the fact that in the electric current the metal of a hydrosol moves toward the positive pole. While the method of Bredig failed to give colloidal mercury, this has been prepared electrolytically by Billitzer[3] by the electrolysis of a very dilute solution of mercurous nitrate with a current of 220 volts at 0.2 to 0.3 amperes. An interesting colloid of silver (and mercury) oxide, under the name of collargol, is prepared by Paal[4] by adding caustic soda to a solution of silver nitrate and sodium protalbinate, or lysalbinate. On warming the solution, colloidal silver is formed, and colloidal gold may be prepared in a similar way. Within the past few months there has been some little discussion as to whether or not the silver in collargol is in chemical combination. The colloidal hydroxides have been studied by Biltz,[5] who prepares them by the dialysis through parchment paper of a dilute solution of the nitrates, the reaction being hydrolytic. Nitrates are chosen from the fact of their lesser influence in promoting the formation of a hydrogel, since some of the acid remains present after dialysis, in the form of a basic nitrate. By a similar method, Melikoff[6] obtains from potassium percolumbate, colloidal percolumbic acid, from which oxygen is evolved on standing, or more rapidly by the addition of concentrated sulphuric acid. This indicates that percolumbic acid is not to be looked upon as a compound of hydrogen peroxide.

But little work has been done upon the inert gases of the atmosphere. By working on a large mass of air (191.1 kg.). Ramsay[7] has studied more completely krypton and xenon, the boiling-points of which are respectively — 151.7° and — 109.1°. The amount of krypton in the atmosphere is estimated as 1 volume in 20,000,000, and that of xenon as 1 volume in

[1] *Ztschr. anorg. Chem.*, **34**, 453; *Ber. d. chem. Ges.*, **35**, 2815, 4066.
[2] *Ber. d. chem. Ges.*, **36**, 609.
[3] *Ibid.*, **35**, 1929.
[4] *Ibid.*, **35**, 2206, 2219, 2224.
[5] *Ibid.*, **35**, 4431.
[6] *J. Russ. Phys.-Chem. Soc.*, **35**, 457.
[7] *Chem. News*, **87**, 159.

170,000,000. By a comparison of the spectra, Liveing[1] concludes that the presence of the inert gases in the sun is exceedingly probable. The spectra of these gases have been more thoroughly studied by Baly,[2] and from the spectra of krypton and xenon it seems probable that some unknown element of higher atomic weight is present.

That subject which has attracted more attention than any other during the past year has, undoubtedly, been radio-activity. Even a brief outline of the work done would require much space, and there may be a question as to how far this subject belongs to chemistry. Two points of interest may, however, be noted. It was recently currently reported that Huggins had found the spectrum of radium to be, in part, identical with that of helium, but this has since proved to be a mistake. It appears, however, that Ramsay has actually obtained helium in the emanations from radium. It also seems, from the most recent reports, that Curie finds the energy of radium to be given off more actively at extremely low temperatures than at higher.

Some little has been done upon the metal-ammonias and metal-ammonium bases. Barium-ammonia has been carefully investigated by Guntz and Mentrel.[3] At temperatures not above 28°, barium unites directly with ammonia, forming the compound $Ba(NH_3)_6$. Below $-23°$ this compound is stable, but above that begins to decompose, forming barium amide, $Ba(NH_2)_2$, which is also formed by the action of ammonia on barium at 280°. At 650° the amide is decomposed into barium nitride, Ba_3N_2. The action is reversible, and below 680° barium nitride unites with ammonium to form the amide. It is worthy of note that by the action of carbon monoxide upon barium-ammonia, barium carbonyl, $Ba(CO)_2$, is formed, a yellow body, fairly stable, but decomposing in the air or moisture. Sodium and lithium form compounds much similar to those of barium. The cesium and rubidium-ammonia have been prepared by Moissan,[4] and have the formula $CsNH_3$ and $RbNH_3$.

The copper-ammonium bases have been the subject of continued investigation by Bouzat.[5] He suggests for the constitution of the three cupri-ammonium bases the following:

$$Cu(NH_3)_2,2HCl;$$
$$Cu(NH,NH_4)_2,2HCl;$$

and

$$Cu(N(NH_4)_2),2HCl,$$

formulae which seem rather a step backward toward the old Blomstrand theory. Several of the metal-ammonium bases have been studied from the standpoint of physical chemistry by Euler[6]

[1] *Proc. Cambr. Phil. Soc.*, **12**, II, 87.
[2] *Proc. Roy. Soc.*, **72**, 84.
[3] *Bull. Soc. Chim.* (3) **29**, 585.
[4] *Compt. Rend.*, **136**, 1177.
[5] *Ann. chim. phys.* (7), **26**, 479; **29**, 305.
[6] *Ber. d. chem. Ges.*, **36**, 1854.

and Bonsdorff.[1] The complex cathions are all strong bases, $Ag(NH_3)_2$ being comparable with the alkalies, its hydroxide being more strongly dissociated than barium hydroxide. The cadmium cathion is $Cd(NH_3)_4$, and that of zinc $Zn(NH_3)_3$. In this connection it may be noted that Bonsdorff obtained argento-cyanic acid, $HAg(CN)_2$, by solution of silver cyanide in HCN and it proves to be a very strongly dissociated acid. Apropos of the Werner hypothesis, Kremann[2] has described an interesting experiment in which the colored complex ions of the luteo-, purpureo- and praseo-cobalt bases migrate to the cathode, while the colored ions of potassium diamino-cobaltonitrite migrate to the anode, as is demanded by the theory. Werner and Goslings[3] discuss the carbonato-cobalt amines, showing that the CO_3 group can enter the co-ordinated nucleus of a molecule, occupying a single co-ordinated position. They, however, seem to assume that it is linked by one unit of combining power to one of the ammonium groups. Several new carbonato-pentamine salts are described by them.

There appears to be a renewed interest of late in those fields which lie in both inorganic and organic chemistry, the organic compounds of inorganic elements. Wyrouboff[4] has examined the didymium and double glucinum oxalates; Guerbet,[5] the lactates of mercury; Buroni,[6] the mercurous and halo-mercurous salicylates; Biilmann,[7] the mercury salts of many other organic acids; Howe and Smiley.[8] chrom-malonic acid and some of its salts; Pictet,[9] acetyl-nitric and acetyl-chromic acids, as well as[10] boro-acetates, boro-butyric acid, etc.; and Pope and Peachy,[11] halo-derivatives of stanni-methane.

In conclusion may be noticed a paper read by Dewar before the Royal Society,[12] giving the density and the coëfficient of expansion of ice, carbon dioxide, hydrated salts, and many other compounds, at low temepratures, generally at about — 188°. The interesting point is brought out that the density of ice never becomes as great as the least density of liquid water, or, as expressed by Dewar, the ice molecules can never approach so near each other by thermic contraction as are the molecules of liquid water.

[1] *Ber. d. chem. Ges.*, **36**, 2322.
[2] *Zischr. anorg. Chem.*, **33**, 87.
[3] *Ber. d. chem. Ges.*, **36**, 2378.
[4] *Bull. Soc. Franc. Min.*, **25**, 66, 71.
[5] *J. Pharm. Chim.* (6), **16**, 5.
[6] *Gazz. chim. ital.*, **32**, II, 305.
[7] *Ber. d. chem. Ges.*, **35**, 2571.
[8] This Journal, **25**, 444.
[9] *Arch. Sci. Geneve*, **15**, 589; *Ber. d. chem. Ges.*, **35**, 2526; **36**, 2215.
[10] *Ber. d. chem. Ges.*, **36**, 2219.
[11] *Proc. Roy. Soc.*, **72**, 7.
[12] *Chem. News*, **85**, 277, 289.

NOTE.

Further Facts Regarding "Ureine."—The September number of the Journal (Review of American Chemical Research, p. 396) gives an abstract of the latest repetition of the "ureine" fallacy, this time published in *Le Physiologiste Russe.*

About three years ago, Dr. William Ovid Moor began his series of communications on "The Discovery of Ureine, the Principal Organic Constituent of Urine and the True Cause of Uraemia."[1] The announcement of the alleged discovery was made in such extravagant terms that it was next to impossible to have any faith in the results and conclusions Dr. Moor brought forward. Thus, "ureine" was said to be the "most characteristic component part of urine," existing in "a quantity superior to urea." "Ureine belongs to the group of alcohols of the aromatic series," wrote Dr. Moor; in another part of the paper it was referred to as "a ferment" with "a potential energy of at least 130° C.," "being the principal cause of the ammoniacal fermentation of urine, as without its presence urea cannot be decomposed into ammonia and carbon dioxide." "Without ureine," it was further stated, "all organic matter would become converted into urea, which would remain in nature without any use, and thus, within a limited period of time, all vegetation and animal as well as human life would cease."

Shortly after Moor's first publication, Chace and I failed completely to obtain any of Moor's essential results, in spite of special care in all our operations. We were able to show, however, that "ureine" is a *mixture* of substances—in fact, merely urine, *minus* most of its water and urea, and some of the other constituents, *plus* material added to and formed in it during the manipulations. Employing customary methods of separation and detection, *purified* "ureine" has been found to contain sodium, potassium, ammonia, phosphate, urea, creatinin, pyrocatechin, phenol-alkaloidal substances and purin bases. Other urinary substances are present, which we have not attempted to identify. Although we avoided excess of mercuric nitrate in the process of decolorization, following Moor's method precisely, we always found mer-

[1] Moor: "The Discovery of Ureine, the Principal Organic Constituent of Urine and the True Cause of Uraemia." Communication presented to the Thirteenth International Medical Congress, Paris, 1900. Published in the *Medical Record*, **58**, 336 (September 1, 1900).

cury in "ureine." Doubtless a soluble compound of mercury was formed in the "purification" process. Nitrate and oxalate, also introduced during this so-called purification, were constant constituents. Shaken repeatedly with excess of ether in a separatory funnel, "ureine" gradually separates into several layers of different color and degrees of transparency, and the ether itself takes on a yellowish tinge. Samples that had been allowed to stand exposed to the air for several months deposited crystals of urea. The amount of ash from four preparations varied from 9 to 24 per cent. A wax-like mass can be obtained immediately on treatment of the "ureine" with concentrated nitric acid. When this mass is broken up mechanically in an excess of nitric acid and examined under the microscope, crystals of urea nitrate are seen to cover the field.

Our general conclusions[1] have been that "ureine" is a *mixture*, containing several of the organic substances, and a considerable proportion of inorganic matter, ordinarily found in normal urine; also matter introduced with reagents in the so-called purification process. Further, the toxicity of "ureine" is due to some of the normal urinary constituents, such as the potassium and the alkaloidal bodies, and to the radicals introduced in "purifying." Consequently, much as it is to be regretted, "ureine" does not furnish a clue to the cause of uraemia nor can any of Dr. Moor's biological deductions regarding "ureine" be accepted.

Our criticism of Moor's work and conclusions in this connection have been endorsed by several investigators, but none of the questions raised by us has ever been answered by Dr. Moor. In the meantime, however, "ureine" is being exploited in the same manner in one journal after another, and impossible chemistry and biology receive wide circulation.

WILLIAM J. GIES.

LABORATORY OF PHYSIOLOGICAL CHEMISTRY
OF COLUMBIA UNIVERSITY.

NEW BOOKS.

THE ELEMENTS OF ELECTRO-CHEMISTRY, TREATED EXPERIMENTALLY. BY DR. ROBERT LÜPKE. Second English edition, translated from the fourth German edition. BY M. M. PATTISON MUIR. 250 pp. Price, $2.50. Philadelphia: J. B. Lippincott Company.

The work is divided into three parts: (1) Recent theories of

[1] Chace and Gies: "Some Facts Regarding 'Ureine,'" *Medical Record*, **59**, 329 (March 2, 1901); also Gies and collaborators: "Biochemical Researches," reprint No. 31 (1903).

electrolysis, 79 pages; (2) the theory of solutions of van't Hoff, 44 pages; (3) the osmotic theory of the current of galvanic cells, 119 pages. Under these headings, Dr. Lüpke has presented, in very readable and easily comprehended language, the present status of the subject. The experimental part is easily the best part of the book, the experiments being very well chosen and very suitable for bringing out the principal facts of the science. If the teacher using the work will confine his pupil's attention to the experiments and the facts which they teach, both teacher and student will be very much helped by the book. If, however, the student wanders into the theoretical part of the book, he will learn, along with much which is good, also much which is questionable, and he will need close attention from his teacher to keep him from receiving distorted ideas. The weak side of the theoretical part is that it presents many of the generalizations of the dissociation theory as if they were without exceptions, and ignores many recent proofs of the failure of the theory in some special cases. Part of Faraday's generalizations are credited to von Helmholtz, simply because, apparently, the latter discussed them in a lecture, while Le Blanc is credited with the discovery of a law regarding the voltage necessary to decompose a compound, which is merely a re-statement of Thomsen's rule, coupled with Hess's law of thermo-neutrality. These, perhaps unconscious, appropriations of electrochemical honors for German scientists will perhaps make the book more popular in Germany, but decrease its reliability for general use.

The translator and publishers have done their work very well.

JOSEPH W. RICHARDS.

ARBEITSMETHODEN FÜR ORGANISCH-CHEMISCHE LABORATORIEN: EIN HANDBUCH FÜR CHEMIKER, MEDIZINER UND PHARMAZEUTEN. VON PROFESSOR DR. LASSAR-COHN. Dritte, vollstandig umgearbeite und vermehrte Auflage. Hamburg und Leipzig: Leopold Voss. 1901–1903. xvi + 1241 pp. Price, 38 marks.

The second edition of this work is well known, both in the original and in the excellent translation of Alexander Smith. The material included in the present edition is more than twice as great as that of the second. The work consists, first, of a "General Part," (213 pages) which discusses general operations such as extraction with ether, distillation, dialysis, sealed tubes, decolorizing of liquids, filtration, crystallization, solvents, determina-

tion of molecular weights, melting-points and boiling-points, sublimation and drying. Methods used in the determination of other physical properties, such as specific gravity, viscosity, heat of combustion, refractive index, specific rotation and electrical conductivity are not mentioned.

The "Special Part" is devoted to a discussion of the more important processes used in the preparation and study of organic compounds, and includes the following topics: Formation of acyl and benzenyl derivatives, and of oximes and hydrazones; fusion with alkalies; introduction of halogens; replacement of halogens; preparation of salts and alkaloids; preparation of diazo compounds; esterification of acids and etherification of phenols; condensation; formation of nitro compounds; separation of isomers; saponification of cyanides and esters. The book concludes with a description of the methods for the ultimate analysis of organic compounds.

As the author of the work points out, the literature of this subject has grown to such overwhelming proportions that it is often extremely difficult to find the method best suited for a particular purpose. The general indexes are usually of little service, since methods of working are, in general, described as incidental to the preparation of some compound, and only the name of the latter is to be found in the index. Professor Lassar-Cohn's book serves a most useful purpose in this direction. The various topics are illustrated by thousands of examples taken from the literature. In the present edition many of these have been taken from the patents, and when we consider the rigid commercial requirement that a method must, if possible, give a good yield, it is easily seen that workers in scientific laboratories may secure very many valuable suggestions from this source.

The experience of the author would seem to have been almost exclusively with aromatic compounds. For this reason the work is somewhat deficient in methods which are especially adapted to aliphatic bodies. English and American journals seem to have been almost completely ignored in the preparation of the book, and in a number of places the author's knowledge is incomplete or one-sided for this reason.

It is very unfortunate that the author has not furnished a general index, which should include all of the compounds men-

tioned in the book. Even the special indexes, at the close of each section, are not so complete as they should be.

In spite of these faults, the book is a very valuable one, and it should be in every laboratory where work in organic chemistry is done. W. A. NOYES.

QUANTITATIVE ANALYSIS, ADAPTED FOR USE IN THE LABORATORIES OF COLLEGES AND SCHOOLS. BY FRANK CLOWES, D.SC., AND J. BERTRAND BERNARD COLEMAN, A.R.C.Sc. Philadelphia: P. Blakiston's Son & Co. 1903. Sixth edition. 602 pp., 125 cuts. Price, $3.50.

This is the sixth edition of a work which, in some one or more of its previous editions, is to be found in most chemical libraries. The main changes are a revision of the section on organic analysis and the addition of methods for the determination of aluminum and nickel in steel, the analysis of aluminum alloys and a table of four-place logarithms. The Gooch crucible is described for the first time, but only in the appendix, and its use is nowhere recommended in the text. The work is still distinctively English and does not always accord with American ideas, or the best and latest practice. This is especially noteworthy in the sections on superphosphates, milk, nitrogen and silicates. The methods given are clearly described and the cross-references are so full and complete that even the routine analyst could scarcely fall into errors of procedure. Little attempt is made, however, to view quantitative analysis from the scientific standpoint.

The book covers a much larger field of analysis than would seem possible from its size. This is due to the fact that there is almost no repetition, and is made possible by the excellent system of cross references already mentioned. The opening descriptive chapters on chemical manipulation are unusually clear and concise. These are followed by numerous, simple gravimetric and volumetric determinations, to be themselves succeeded by a long list of general quantitative analyses covering a wide field.

The book will be found useful in all laboratories and will be serviceable to students under proper guidance. It is well printed and has a good index. C. L. PARSONS.

THE SUGAR-CANE IN EGYPT. BY WALTER TIEMANN, Member of the Society of German Sugar Technicists and of the Association des Chimistes de Sucreries et Distilleries, Paris. x + 74 pp. Price, 5/- net.

This work, by the director of the experimental station in Upper Egypt, treats of the sugar-cane industry only from the agricul-

tural standpoint and in such a manner as to excite nothing but admiration for the scientific exactness with which the experiments in intensive culture were prosecuted. It is shown that modern methods must supplant the Arabs' indifference to the basic rules of rational cultivation.

The author discusses depletion of soil by a defective tenant system, best native cane varieties, details of cane selection, planting, cultivation and harvest, proper conditions of the seasons and prevailing meteorological conditions. The five years of experimental work were controlled by digestion analyses of the canes, systematically tabulated. Alluvial, coal and limestone deposits are described and their analyses given. We find excellent, practical information regarding native manures, such as stable dung, "ruins manures," zebach balladi, dove guano, bat guano and their accumulation, with analyses. The author states a need for imported artificial fertilizers and green manures, and adds practical formulae of tried fertilizer combinations, with cost and returns.

The instructions for carrying out the system for a manurial experiment, as adopted by Dr. Weitz, secretary to the Delegation of the United Association of Saltpeter Manufacturers in Berlin, embody some most practical suggestions, if accurate deductions are to be made.

Chapters VII and VIII, 27 pages, present the manurial experiments in detail, comprising acreage, character of cane produced, fertilizer applied, crop yield and cane analyses; *i. e.*, sp. gr., Beaumé, Brix, juice per cent., non-sugar, quotient, sucrose, glucose and weight.

The material is well arranged, amply illustrated and fully supplemented by plotted tables. The style is very lucid and the presentation is shorn of unnecessary detail. D. L. DAVOLL, JR.

Index to Volume XXV, 1903.

ABEL test, for explosives..... 549
ABRAHAM, HERBERT. A modification of the Babcock-Blasdale viscosity test for olive oil, 968; See H. C. Sherman.
Acids, derivatives of complex inorganic.....298, 1223, 1227, 1229
Acylamidines, molecular rearrangement of unsymmetrical..... 787
Adhesion, study of..... 186
Adlumia cirrhosa, alkaloids of..... 596
Adlumidine, in Adlumia cirrhosa..... 599
Adlumine, in Adlumia cirrhosa..... 598
AFFELDER, O. I. See H. E. Walters.
Aldehyde condensation products of arylpseudothiohydantoins..... 366
Alakali, determination in soils..... 496
Alkaloids, double halides with tellurium, 730; Of Adlumia cirrhosa, 596; Of isopyrum and isopyroine..... 99
Alkylthioketodihydroquinazolines, synthesis..... 372
ALLAN, F. B. The basic oxalates of bismuth..... 722
ALLEN, E. T. Precipitation and separation by weak organic bases..... 421
Aluminum, separation from iron..... 423
Adluminum phosphate, dehydrated, effect of moisture on availability of..... 280
Amandin..... 845
Amines, aromatic, action of 3-nitrophthalyl chloride with..... 601
p-Aminobenzonitrile..... 478
Aminomethyl phenylether..... 62
Ammonia, action of 3-nitrophthalyl chloride with, 601; Electrolytic reduction of nitric acid to, 1042; Fixation by Hawaiian soils..... 47
Ammonium: aluminico-tungstate, 1230; Bismuthico-tungstate, 1232; New double oxalate with bismuth, 729; Sulphate, precipitation limits of vegetable proteins with, 837; Vanadico-tungstate, 1227; Vanadoso-tungstate..... 1228
Ammonio-silver compounds in solution..... 69
Analyses of materials for Portland cement..... 1180
ANDREWS, LAUNCELOT W. Titrations with potassium iodate..... 756
Aniline, action on phthalyl and succinyl chlorides, 612; Hydrolysis..... 433
Aniline hydrochloride, action of sodium salts of dibasic acids on..... 612
Aniline method for formaldehyde..... 1033
Anthranilic nitrile, syntheses with..... 372
Antimony, rapid electrolytic precipitation, 905; Separation of mercury from..... 198
Arnold method for titanium..... 1083
Arsenic, new complex acids of, 306ff; Separation of mercury from, 198; Trioxide in Paris green, modification of Avery-Beans method..... 963
Arsenious acid, determination in Paris green..... 1096
Arylpseudothiohydantoins, aldehyde condensation products of..... 366
Asbestos muffle..... 1277
Atomic weights, report of International Committee, 1; Tenth Annual Report of Committee on..... 223
ATWATER, W. O., and J. F. Snell. Description of a bomb-calorimeter and method of its use..... 659
AUCHY, GEORGE. Rapid determination of molybdenum in steel, 215; Rapid determination of phosphorus in steel..... 772
Avery-Beans method for arsenious acid, 1096; Modification of,..... 963
Azophthalic acid..... 768

BABCOCK-BLASDALE test, modification of..... 968
Bacilli, tubercle, composition of, from various animals..... 354
BAIN, J. W. The estimation of titanium..... 1073

BALKE, CLARENCE W., and E. F. Smith. Derivatives of complex inorganic acids.. 1229
BALL, S. See E. D. Campbell.
Barium sulphate and adhesion..... 186
Bases, weak organic, precipitation and separation by..... 421
BASKERVILLE, CHARLES. Mercurous sulphide..... 799
Baskerville method for titanium..... 1075
Bearing metals, analysis of..... 632
BENEDICT, STANLEY, and J. F. Snell. A method for the estimation of chlorides, bromides and iodides..... 1138
Benzene, determination in illuminating gas..... 503
BEST, ALFRED. See Charles E. Coates.
Bibromaminobenzoic acid..... 935
Bicarbonates, Perkin's test..... 537
Biochemisches Centralblatt..... 322
Bismuth, analysis of ores, 916; Basic oxalates, 722; Electrolytic estimation and separation, 83; New double oxalates, 728, 729; Rapid electrolytic precipitation, 901; Separation from copper, 907, 915; Volumetric determination as molybdate 907
Bismuth ammonium molybdate..... 919
Blank-Finkenbeiner method for formaldehyde..... 1029
BLASDALE, W. C. On ceroptene, a new organic compound..... 1141
BOGERT, MARSTON T. Normal heptyl thiocyanate, etc..... 289
BOGERT, MARSTON T., H. C. Breneman and W. F. Hand. Synthesis of alkylthioketodihydroquinazolines 372
BOGERT MARSTON T., and Lothair Kohnstamm. *p*-Aminobenzonitrile..... 478
BOGERT, MARSTON T., and W. F. Hand. 3,5-Bibrom-2-aminobenzoic acid: its nitrile and the synthesis of quinazolines from the latter..... 935
Bomb-calorimeter, description of..... 659
Bone-ash, experiments with..... 820
BOSWORTH, A. W. A burette, etc., for Kjeldahl nitrogen determinations..... 535
"Break" from linseed oil, composition of..... 716
BRENEMAN, H. C. See Marston T. Bogert.
Bromides, detection of, in presence of chlorides and iodides, 809; Estimation in presence of chlorides and iodides..... 1138
Bromotellurates 732
Bronze, analysis of..... 632
BROWN, LOUISE. See C. F. Roberts.
BROWNE, C. A., JR. A contribution to the chemistry of rice oil, 948; Additional note on the filtration of crude fiber, 315; The effects of fermentation on composition of cider, etc..... 16
Bumping, prevention of..... 163
BURKE, EDMUND. See F. W. Traphagen.

CADMIUM, rapid electrolytic precipitation, 902; Separation of bismuth from.. 93
Calcium, atomic weight, 225; Electrolytic production, 873; Precipitation by sodium carbonate..... 732
Calorimeter. See Bomb-calorimeter.
CAMERON, F. K., and G. H. Failyer. The determination of small amounts of potassium in aqueous solutions..... 1063
CAMPBELL, E. D., and S. Ball. An experiment upon the influence of the fineness of grinding upon the clinkering of Portland cement..... 1103
Carbohydrate group in the protein molecule..... 474
Carbon, combustion in platinum crucible, 237, 997; In iron, effect on test for tin.. 876
Carbon dioxide, determination of atmospheric..... 150
Carbon monoxide, reducing action on metallic oxides..... 641
Carbonic acid, determination in drinking-water..... 742
Casein, effect of enzyme on.....1249 ff
Cathodes, mercury, in electrochemical analysis..... 883
Cerium, and phenylhydrazine, 429; Behavior toward organic bases..... 1128

Ceroptene 1141
Cerotic acid 1151
CHAMBERS, VICTOR J. 3-Nitrophthalyl chloride and its action with ammonia, etc.. 601
Cheese, effect of rennet enzyme on proteids of 1243
Chemicals, investigation of purity of 548
Chemistry, inorganic, review of recent work in, 1282; Of fatgue 33
Chlorides, detection of, in presence of bromides and iodides, 809; Estimation in presence of bromides and iodides 1138
Chlorotellurates 731
Choke-damp, new apparatus for examination of 534
Cholesterol, in maize oil, 251; In olive oil 498
Chromium, separation of bismuth from 94
Chrom-malonates 444
Cider, effect of fermentation on composition 16
Cinnabar, analysis of 207
CLARKE, FRANK W. Report of the International Committee on Atomic Weights, 1; Tenth Annual Report of Committee on Atomic Weights 223
Clay, cause of plasticity 451
Coal, determination of sulphur in, 184; Rapid method for sulphur in 1265
Coal oils, testing of 814
Coal tar, testing of 814
COATES, CHARLES E., and Alfred Best. The hydrocarbons in Louisiana petroleum 1153
Cobalt, rapid electrolytic precipitation, 901; Separation of bismuth from 95
COHEN, LILLIAN. See E. P. Harding.
Coke, determination of sulphur in 184, 1265
Colorimetric determination of phosphates, 1056; Of potassium 990
Color test in high carbon steels 999
Combustions, carbon, platinum crucible for 237
Conductivity of hydrogen ion 165
Conglutin 339
COOK, ALFRED N. Derivatives of phenylether, V 60
Copals, chemical constants of ..... 861 ff
Copper, rapid electrolytic precipitation, 897; Separation from nickel, 905; Separation from zinc, 907; Separation from selenium and tellurium, 895; Separation of bismuth from, 907, 915; Separation of mercury from 198
Copper matte, analysis of, for bismuth 917
Corn kernel 1166, 1236
Corylin 341, 845
COX, ALVIN J. See J. M. Stillman.
CRAMER, W. B. See article by Treat B. Johnson 491
CRAMPTON, CHARLES A. The composition of process or renovated butter 358
CRAWLEY, J. T., and R. A. Duncan. Fixation of ammonia and potash by Hawaiian soils 47
Crude fibre, filtration of 315
CUMMER, FREDERICK W. See Frederick L. Dunlap.
Cyanides, double, of zinc with sodium and potassium 570

DAMAR 869
DAVIS, G. T. See M. Gomberg.
DAVOLL, DAVID L. A study of raffinose determinations 1019
DEMPWOLF, C. H., JR. A process for making available phosphates 818
DENNIS, L. M., and J. G. O'Neill. The determination of benzene in illuminating gas 503
DE SCHWEINITZ, E. A., and M. Dorset. The composition of the tubercle bacilli, etc. 354
Dimethylcyanadipic ester 1096
Dimethyldibenzylamine 1091
Dimethylbenzaldazine 1091
Dinitromethyl phenylether 63

Dithiocarbamic acid, some new alkyl esters of..... 289
Donnan, F. G. On the emulsifying action of soap..... 1215
Dorset, M. See E. A. De Schweinitz.
Duncan, R. A. See J. T. Crawley.
Dunlap, Frederick L., and F. D. Shenk. A preliminary report upon the oxidation of linseed oil..... 826
Dunlap, Frederick L., and F. W. Cummer. The action of the sodium salts of dibasic acids on aniline hydrochloride, etc..... 612
Dunnington, F. P. A convenient form of table for calculation of chemical weights..... 537

EAST, E. M. See C. G. Hopkins.
Edestin.....332, 843
Electric test retort..... 415
Electrolytic determination of bismuth, 83; Of manganese..... 1045
Electrolytic precipitation of nickel..... 1039
Electrolytic production of calcium..... 873
Electrolytic reduction of nitric acid..... 1042
Electrons..... 405
Emulsions..... 516
Enzymes of rennet extract..... 1243
Errata..... 882
Excelsin..... 843
Explosion test..... 552
Explosives, nitrocellulose, stability test..... 549

FAILYER, G. H. See F. K. Cameron.
Fatigue, contribution to the chemistry of..... 33
Fats, iodine absorption of..... 244
Fay, Irving W., and A. F. Seeker. Reducibility of some metallic oxides by hydrogen, etc..... 641
Fermentation, effect of, upon composition of cider and vinegar..... 16
Ferric salts and phenylhydrazine..... 430
Fertilizers, determination of potash in..... 416
Fire-proof wood, method of testing..... 406
Forbes, Fred B., and G. H. Pratt. The determination of carbonic acid in drinking-water..... 742
Formaldehyde, comparison of methods for determining, 1028; Estimation in milk..... 1036
Fossil resins, chemical constants..... 860
Frank, Henry. See E. H. Miller.
Frankforter, George B. The alkaloids of isopyrum and isopyroine..... 99
Frear, W., and C. P. Beistle. Some Cuban soils of chemical interest..... 5
Freezing-points of dilute solutions..... 291
Fuller, Myron L. Etching of quartz in the interior of conglomerates..... 153

GAS, illuminating, determination of benzene in, 503; Mine, new apparatus for examination of..... 534
Geromanos, H. W. See G. W. Rolfe.
Gies, William J. Further facts regarding "ureine"..... 1280
Gill, Augustus H., and Charles G. Tufts. Does cholesterol occur in maize oil? 251, 498; Sitosterol, a possible test for maize oil..... 254
Gliadin..... 847
Globulin, flaxseed, 844; Squash-seed, 844; Walnut.....846, 848
Glucose, commercial, determination in molasses, etc..... 982
Gold, fluoride of, 1136; Rapid electrolytic precipitation..... 905
Gomberg, M. On the possible existence of a class of bodies analogous to triphenylmethyl..... 1274
Gomberg, M., and G. T. Davis. On triphenylmethyl acetate..... 1269

GOODWIN, JOSEPH H. The electrolytic production of calcium..... 873
Graphite muffle..... 1277
GROSS, ABRAHAM. Purification and estimation of iodine..... 987
Guttmann test, for explosives..... 551

HADDOCK, ISAAC T. See G. W. Rolfe.
Halogens, estimation of, when together..... 1138
HAND, WILLIAM F. See Marston T. Bogert.
HANN, FRANK L. A cheap and efficient water-blast..... 770
HARDING, EVERHART P., and L. Cohen. Reduction of 2,5-dimethylbenzaldazine and the preparation of some of its salts..... 1063
HARDING, H. A. See L. L. Van Slyke.
HARE, C. The determination of potash in fertilizers, etc..... 416
HARPER, HENRY W., and Margaret Holliday. Contribution to the chemistry of fatigue..... 33
HARRIS, ISAAC F. See Thomas B. Osborne
HART, EDWIN B. See Lucius L. Van Slyke.
HARTWELL, BURT L. The behavior of cerium, lanthanum, neodymium, praseodymium, thorium and zirconium toward organic bases..... 1128
HAYWOOD, J. K. A modification of the Avery-Beans method for determining total arsenious oxide in Paris green..... 963
HENDRIXSON, W. S. Silver as a reducing agent..... 637
Heptane, bromination of..... 532
Heptyl thiocyanate, normal..... 289
Hess test, for explosives..... 552
Hexamethylenetetramine method for formaldehyde..... 1030
Hexanitromethyl phenylether..... 64
Hilger-Haas method for titanium..... 1086
HILL, LUCIAN A. A colorimetric method for the determination of small quantities of potassium..... 990
HILLEBRAND, W. F. Critical review of the second series of analyses for material for the Portland cement industry, etc..... 1180
HILLYER, H. W. A method of grading soaps as to their detergent power, 1256; A study of soap solutions, 524; On the cleansing power of soap..... 511
Hoitsema test, for explosives..... 552
HOLLIDAY, MARGARET. See Henry W. Harper.
β-Homochelidonine, in Adlumia cirrhosa..... 598
Honey, determination of glucose in..... 982
HOPKINS, C. G., L. H. Smith and E. M. East. The chemical composition of different parts of the corn kernel..... 1166
HOWE, JAMES L. Chrom-malonates, 444; Review, recent work in inorganic chemistry..... 1282
Hydantoin, derivatives of..... 366
Hydrocarbons of Louisiana petroleum..... 1153
Hydrocyanic acid in sorghum..... 55
Hydrogen, reducing action on metallic oxides..... 641
Hydrogen ion, equivalent conductivity..... 165
Hydrogen sulphide, distribution to laboratory classes..... 231
Hydrolysis of starch by acids..... 1003

INDICATORS, theories of..... 1112
Inorganic chemistry, review of recent work in..... 1282
Iodides, detection of, in presence of chlorides and bromides, 809; Estimation in presence of chlorides and bromides..... 1138
Iodine, atomic weight, 223; Probable cause of different colors of, 50; Purification and estimation..... 987
Iodine absorption of oils and fats..... 244
Iodometric method for formaldehyde..... 1031

Iron, corrosion, 394; effect of combined carbon in, on test for tin, 876; Rapid electrolytic precipitation, 903; Separation of bismuth from, 97; Separation of manganese from..... 1049
Iron and steel, permanent protection of, 761; Volumetric determination of manganese in..... 392
Isoamyl chloride, action of fuming sulphuric acid on..... 932
Isoapiol, derivatives of..... 262
Isopyroine, alkaloids of..... 99
Isopyrum, alkaloids of..... 99
Isosafrol, derivatives of..... 262

JAMIESON, GEORGE S. See Henry L. Wheeler.
JAYNE, H. W. Testing of coal tar and oils and an improved testing still..... 814
JOHNSON, TREAT B. On the molecular rearrangement of thiocyanacetanilides, etc. 483
Juglansin..... 853

KAHLENBERG, LOUIS. Action of metallic magnesium on aqueous solutions..... 380
KAMMERER, ALFRED L. The electrolytic estimation of bismuth, etc..... 83
KELLER, HARRY F. On the occurrence of alum as an efflorescence on bricks..... 214
KOHNSTAMM, LOTHAIR. See Marston T. Bogert.

LACHMAN, ARTHUR. A probable cause of the different colors of iodine solutions..... 50
Lanthanum, atomic weight, 227; Behavior toward organic bases..... 1128
LEACH, ALBERT E. The determination of commercial glucose in molasses, syrups and honey..... 982
Lead, rapid electrolytic precipitation..... 904
Lead halides, solubility in water..... 469
Lecture experiment..... 996
Legler method for formaldehyde..... 1030
Legumelin..... 337
Legumin..... 335, 847
LENHER, VICTOR. Fluoride of gold..... 1136
LENHER, VICTOR, and W. Titus. Double halides of tellurium with the alkaloids..... 730
Leucosin..... 338
LICHTY, D. M. The solubility of the bromide, etc., of lead in water..... 469
Life history of a doctrine..... 115
Limestones, chemical method for determining quality..... 143
LIND, S. C. The constitution of potassium ruthenium nitrosochloride in aqueous solution..... 928
Linseed oil, composition of "break" from, 716; Oxidation of..... 826
Lipase in rice bran..... 950
LONG, J. H. On the relation of the specific gravity of urine to the solids present..... 257, 871
Lunge-Trillich method..... 749

MAGNESIUM, action on aqueous solutions, 380, 801; Precipitation by sodium carbonate..... 732
Magnesium hydroxide and adhesion..... 186
Maltose, presence in acid-hydrolyzed starch products..... 1015
Manganese, electrolytic determination, 1045; Separation from iron and zinc, 1045; Separation of bismuth from, 96; Volumetric determination in iron and steel. 392
Manganese hydroxide and adhesion..... 186
Massecuite..... 858
McFARLAND, DAVID F. See H. L. Wheeler.
McFARLAND, D. F. See article by Treat B. Johnson..... 488
McINTOSH, D. A lecture experiment with an undissociated salt..... 996

McKenna, Charles F. An electric test retort, 415; A proposed method of testing wood treated to resist fire..... 406
Melcher, A. C. See W. R. Whitney.
Melting-point determinations, liquid baths for..... 161
Mercurous sulphide..... 799
Mercury, cathode, 883; Determination and separation, 198; Oxides, reduction of, 645; Rapid electrolytic precipitation, 901; Separation from selenium and tellurium..... 894
Metals, delicacy of tests for, 992; Electrolytic separation of, 892; Rapid electrolytic precipitation..... 896
Methyl acetate, saponification..... 435
β-Methyl adipic acid, synthesis of..... 1093
Methylcyanadipic ester..... 1095
Milk, composition of cows', 132; Effect of rennet enzyme on proteids of, 1243; Estimation of formaldehyde in..... 1036
Miller, Edmund H., and H. Frank. On the reduction of molybdenum by zinc and the ratio of bismuth to molybdenum in bismuth ammonium molybdate... 919
Molasses, determination of glucose in..... 982
Molybdate method, for bismuth..... 911
Molybdenum, rapid determination in steel, 215; Rapid electrolytic precipitation, 904; Reduction by zinc..... 919
Moore, F. J. Some derivatives of *p*-sulphocinnamic acid..... 622
Morse, Fred W. The effect of moisture on the availability of dehydrated phosphate of alumina..... 280
Muffle, an efficient..... 1277
Munson, L. S. See L. M. Tolman.
Munson, L. S., and L. M. Tolman. The composition of fresh and canned pineapples..... 272
Myrtle wax, constants and composition..... 629

Neodymium, behavior toward organic bases..... 1128
New apparatus..... 534, 535
New Books. A catalogue of the Library of the Chemical Society (of London), 658; A Course in Modern Analysis (E. H. Whittaker), 220; A Course in Qualitative Analysis (F. P. Venable), 4th ed., 219; A History of Hindu Chemistry from the Earliest Times, etc. (P. C. Ray), 650; A Laboratory Outline of General Chemistry (Alexander Smith), 321; Analytical Chemistry, Vol. I (trans. Wm. T. Hall), 1097; An Introduction to Chemistry (D. S. MacNair), 317; Annuaire pour l'An. 1903 (pub. Paris), 658; Arbeitsmethoden für Organisch-Chemische Laboratorien (Prof. Lassar-Cohn), 3d ed., 1297; A Text-Book of Organic Chemistry (A. F. Holleman), 655; A Text-Book of Organic Chemistry (W. A. Noyes), 774; A Text-Book of Quantitative Chemical Analysis (Frank Julian), 318; A Text-Book of Volumetric Analysis (H. W. Schimpf), 880; Botany and Pharmacognosy (Henry Kraemer), 541; Chemisches Practicum, I Teil (A. Wolfrum), 107; Chemistry by Observation, Experiment, and Induction (J. I. D. Hinds), 317; Chemistry of the Dyestuffs (G. von Georgievics, trans. C. Salter), 1216; Des Industries Chimiques et Pharmaceutiques (Albin Haller), 1000; Descriptive Chemistry (L. C. Newell), 1220; Determination of Radicals in Carbon Compounds (H. Meyer), 780; Die Constitution des Kamphers und Seiner Wichtigsten Derivate (Ossian Aschan), 1100; Die Zersetzung Stickstofffreier Organischer Substanzen durch Bakterien (O. Emmerling), 217; Disinfection and Disinfectants (M. J. Rosenau), 217; Electro-Chemical Analysis (E. F. Smith), 218; Elementary Chemistry (L. M. Dennis and F. W. Clarke), 215; Elementary Chemistry (R. H. Bradbury), 773; Elements of Inorganic Chemistry (H. C. Jones), 1300; Elements of Physics (E. J. Andrews and H. N. Howland), 654; Essays in Historical Chemistry (T. E. Thorpe), 106; First Book of Qualitative Chemistry, etc. (Prescott and Sullivan), 108; Galvanic Batteries: Their Theory, Construction and Use (S. R. Bottone), 222; G. Bunge's Physiological

and Pathological Chemistry (trans. F. A. Starling), 218; General Principles of Physical Science (A. A. Noyes), 221; Higher Mathematics for Students of Chemistry and Physics (J. W. Mellor), 103; India Rubber and Gutta Percha (trans. J. G. McIntosh), 785; Inorganic Chemistry Syllabus (H. C. Carel), 540; International Catalogue of Scientific Literature—Chemistry, Part I., 111; Kalender fur Electrochemiker, etc. (ed. A. Newburger), 541; Laboratory Exercises in Physics for Secondary Schools (G. R. Twiss), 222; L'Acetylene. Theorie. Applications (Marie-Auguste Morel), 1101; Lead Smelting (M. W. Iles), 449; Les Derives Tartriques du Vin (P. Carles), 3d edition, 1218; Logarithmische Rechentafeln für Chemiker (F. W. Kuster), 109; Lois Generales de L'Action des Diastases (Victor Henri), 780; Lead and Its Compounds (Thomas Lambert), 653; Notes on Metallurgical Analysis (N. W. Lord), 776; Notions Fondamentales de Chemie Organique (Ch. Moureau), 316; Œuvres Completes de J. C. Galissard de Marignac, Tome I., 320; On the "Beckmann Rearrangement" (Julius Stieglitz), 649; Papers on Etherification, etc. (A. W. Williamson), Alembic Club Reprint, 548; Physical Chemistry for Physicians and Biologists (Dr. E. Cohen), 777; Physico-Chemical Tables for the Use of Analysts, Physicists, etc. (J. Castell-Evans), 657; Physics—Text-Book for Secondary Schools (F. Slate), 106; Principles of Dyeing (G. S. Fraps), 544; Principles of Inorganic Chemistry (H. C. Jones), 538; Qualitative Analysis, etc. (Dennis and Whittelsey), 112; Quantitative Analysis—Adapted for Use in the Laboratories of Schools and Colleges (F. Clowes and J. B. B. Coleman), 1299; Quantitative Chemical Analysis by Electrolysis (Prof. A. Classen), 776; Quantitative Classification of Igneous Rocks (Whitman Cross, *et al.*), 319; Radium and Other Radio-active Substances, etc. (W. J. Hammer), 1099; Recipes for the Color, Paint, Varnish, etc., Trades, 219; Reflexions sur la Puissance motrice du Feu, et sur les Machines propres a devellopper cette Puissance (Sadi Carnot), 784; Sealing-Waxes, Wafers, and Other Adhesives (H. C. Standage), 545; Siderology: The Constitution of Iron Alloys and Slags (H. F. von Jüptner), 655; Simple Methods for Testing Painters' Materials (A. C. Wright), 1221; Technical Mycology: The Utilization of Micro-organisms in the Arts and Manufactures, (F. Lafar), 783; Tests and Reagents, Chemical and Microscopical, etc. (A. I. Cohn), 653; Text-Book of Electrochemistry (S. Arrhenius), 104; The American Year-Book of Medicine and Surgery, Vol. I., General Medicine (pub. W. B. Saunders & Co.), 784; The Analysis of Oils and Allied Substances (A. C. Wright), 649; The Analysis of Steel Works Material (Brearley and Ibbotson), 109; The Chemical Technology of Textile Fibres (Georg von Georgievics), 543; The Chemistry of Pigments (E. J. Parry and J. H. Coste), 877; The Dyeing of Woolen Fabrics (Franklin Beech), 544; The Electro-Plating and Electro-Refining of Metals (Watt and Philip), 102; The Elements of Electro-Chemistry, Treated Experimentally (Robt. Lupke, trans. M. M. P. Muir), 2d English edition from 4th German, 1297; The Elements of Physics (Nichols and Franklin), 113; The Praxis of Urinary Analysis, (trans. Dr. H. W. F. Lorenz), 880; The Principles of Animal Nutrition with Special Reference to the Nutrition of Farm Animals (H. P. Armsby), 782; The Principles of Leather Manufacture (H. R. Procter), 878; The Sugar-Cane in Egypt (Walter Tiemann), 1300; The Teaching of Chemistry and Physics in the Secondary School (Smith and Hall), 447; The Testing of Chemical Reagents for Purity (C. Krauch), 3d edition trans., 652; The Utilization of Waste Products (Theodore Koller), 546; The Utilization of Wood Waste (Ernst Hubbard), 547; Thonindustrie-Kalender, 1903, 448; Traité de Chimie Physique—Les Principes (Jean Perrin), 779; Vorlesungen ueber Theoretische und Physikalische Chemie (J. H. van't Hoff)..... 654

Nickel, electrolytic precipitation, 899, 1039; Separation from copper, 905; Separation of bismuth from..... 95

NIKAIDO, Y. Coloring-matter in yellowish gray sugar..... 857

Nitrates, reduction of nitric acid in..... 1042

Nitric acid, electrolytic reduction to ammonia..... 1042

Nitrocellulose powders, new stability test..... 549
Nitrogen, in protein bodies, 323; Kjeldahl method, burette, etc., for..... 535
Nitromethyl phenylether..... 60
Nitrophthalamic acids..... 767
Nitrophthalanilic acids..... 767
Nitrophthalic acid..... 767
3-Nitrophthalyl chloride, action with ammonia and amines..... 601
Noyes, A. A. The equivalent conductivity of the hydrogen ion, etc., II..... 165

OAT kernels..... 1237
Oil, linseed, composition of break from, 716; Linseed, oxidation of, 826; Maize, occurrence of cholesterol in, 251; Maize, sitosterol a test for, 254; Olive, occurrence of cholesterol in, 498; Olive, 954; Olive, substitutes for, 954; Olive, viscosity test, 968; Rice, contribution to chemistry of, 948; See Petroleum.
Oil analysis, viscosity of the soap solution..... 977
Oils, constants of various, 960; Fatty, influence of atmospheric oxidation on, 711; Iodine absorption of..... 244
Olive oil, pure California, table, 956, 957; pure Italian, table, 958; Substitutes for, 954; Viscosity test..... 968
O'Neill, Edmond. Petroleum in California..... 699
O'Neill, J. G. See L. M. Dennis.
Osborne, Thomas B. The specific rotation of the nucleic acid of the wheat carbohydrate group in the protein molecule, 474; The globulin of the English walnut, the American black walnut and the butternut, 848; The precipitation limits with ammonium sulphate of some vegetable proteins, 837; The specific rotation of some vegetable proteins, 842; The tryptophane reaction of various proteins..... 853
Oxygen, preparation of..... 876

PARIS green, determination of arsenious acid in, 1096; determination of total arsenious oxide..... 963
Parsons, Charles L. The distribution of hydrogen sulphide to laboratory classes..... 231
Patten, Harrison E. A study of magnesium and manganous hydroxides, etc... 186
Pennock, J. D., and D. A. Morton. A rapid method for sulphur in coal and coke 1265
Pepsin, commercial effect on cheese ripening..... 1247
Perkin's test for bicarbonates..... 537
Peter, Alfred M. A chemical method for determining the quality of limestones, 143
Petroleum, in California, 699; Louisiana, hydrocarbons in..... 1153
Pettenkofer method..... 743
Pettit, J. H. Improved method for separation, etc., of total alkalies in soils.... 496
Phaseolin.....336, 847
Phenylamidines, substituted..... 739ff
Phenylcyanguanidine..... 721
Phosphate rock, experiments with..... 822
Phosphates, colorimetric estimation of, in presence of silica, 1056; Process for making available..... 818
Phosphoric acid, determination in soils, 491; Determination of small quantities.. 169
Phosphorus, determination of, in bronzes, 634; New complex acids of, 298; Rapid determination in steel..... 772
Phthalyl chloride, action of aniline on..... 620
Pickel, J. M., and C. B. Williams. An efficient asbestos or graphite muffle..... 1277
Pineapples, composition of..... 272
Plasticity of clays, cause of..... 451
Platinum, combustion of carbon in..... 997
Platinum crucible for carbon combustions..... 237
Pond, F. J., and C. R. Siegfried. Derivatives of isosafrol and isoapiol..... 262

Portland cement, critical review of analyses of materials, 1180; Influence on fineness of grinding on clinkering..... 1103
Potash, determination in fertilizers, 416; Determinations in soil, 491; Fixation by Hawaiian soils..... 47
Potassium, colorimetric determination of, 990; Determination of small amounts, 1063; New double oxalate with bismuth..... 728
Potassium bismuthico-tungstate..... 1233
Potassium cyanide, method for formaldehyde..... 1032
Potassium iodate, titrations with..... 756
Potassium ruthenium nitrosochloride..... 928
Potassium zinc cyanide..... 570
Potato tubers..... 1239
Praseodymium, behavior toward organic bases..... 1128
PRATT, GILBERT H. See F. B. Forbes.
Precipitation by weak organic bases..... 421
PRETZFELD, CHARLES J. The gravimetric determination of mercury, etc..... 198
Protein molecule, carbohydrate group in..... 474
Proteins, nitrogen in, 323; Tryptophane reaction, 853; Vegetable, precipitation limits with ammonium sulphate, 837; Vegetable, specific rotation..... 842
Protopine in Adlumia cirrhosa..... 597
Prussic acid. See Hydrocyanic acid..... 55
Pseudothiohydantoins, molecular rearrangement..... 483
Pseudothioureas, described as normal ureas..... 719

QUINAZOLINES, synthesis of..... 935

RADIUM, atomic weight..... 230
Raffinose determinations..... 1019
Reducibility of some metallic oxides by hydrogen and carbon monoxide..... 641
REMSEN, IRA. The life history of a doctrine..... 115
Rennet enzyme, effect on proteids of milk and cheese..... 1243
Resin, fossil, chemical constants of..... 860
Respiration calorimeter..... 698
Retort, an electric test..... 415
Rice oil, contribution to chemistry of..... 949
RICHARDS THEODORE W. Note concerning the calculation of thermochemical results, 209; The freezing-point of dilute solutions..... 291
RIEDERER, HERMAN S. The volumetric determination of bismuth as molybdate and its separation from copper..... 907
ROBERTS, CHARLOTTE F. and L. Brown. The action of metallic magnesium upon aqueous solutions..... 801
Rock powders, cause of cementing value..... 451
ROGERS, ALLEN. Derivatives of new complex inorganic acids..... 298
ROGERS, ALLEN and E. F. Smith. Derivatives of complex inorganic acids, III, 1223; IV, 1227.
ROLFE, GEORGE W. and H. W. Geromanos. Notes on the hydrolysis of starch by acids..... 1003
ROLFE, GEORGE W. and I. T. Haddock. The presence of maltose in acid-hydrolyzed starch products..... 1015
Ruthenium, double salt with potassium..... 928

SALICYLIC acid, occurrence in fruits..... 242
Salt, common, effect on action of rennet enzyme..... 1252
SCHLOTTERBECK, J. O., and H. C. Watkins. The alkaloids of Adlumia cirrhosa, (2nd paper)..... 596
SCHOLL, G. P. The electrolytic determination of manganese and its separation from iron and zinc..... 1045
SCHREIBER, F. New apparatus for the examination of choke-damp, etc..... 534

SCHREINER, OSWALD. On a colorimetric method for the estimation of phosphates in the presence of silica..... 1056
SCUDDER, HEYWARD. Liquid baths for melting-point determinations, 161; The prevention of bumping..... 163
SEEKER, ALBERT F. See Irving W. Fay.
Selenium, atomic weight..... 225
Seyler method..... 749
SHARWOOD, W. J. A study of the soluble cyanides of zinc with potassium and with sodium..... 570
SHENK, FRANCIS D. See F. L. Dunlap.
SHERMAN, H. C. On the composition of cows' milk, 132; On the influence of diet, muscular exertion, and loss of sleep upon the formation of uric acid in man..... 1139
SHERMAN, H. C. and H. Abraham. The viscosity of the soap solution as a factor in oil analysis..... 977
SIEGFRIED, C. R. See F. J. Pond.
Silica, determination of small quantities, 169; Estimation of phosphates in presence of..... 1056
Silver, as a reducing agent, 637; Compounds with ammonium, 69; Rapid electrolytic precipitation, 900; Separation from selenium, 892; Separation from tellurium..... 893
Silver ammonium aluminico-tungstate..... 1231
Silver oxide, reduction of..... 642
Sitosterol, a possible test for maize oil..... 254
SLADE, HENRY B. Prussic acid in sorghum..... 55
SMITH, BERNARD H. The estimation of formaldehyde in milk..... 1036
SMITH, EDGAR F. See Allen Rogers; See Clarence W. Balke.
SMITH, L. H. See C. G. Hopkins.
SMITH, WARREN R., and Frank B. Wade. The analytical constants and composition of myrtle wax..... 629
SNELL, J. F. See Stanley Benedict; See W. O. Atwater.
Soap, cleansing power, 511; Emulsifying action of, 1215; Grading as to detergent power..... 1256
Soap solutions, a study of, 524; Viscosity of, in oil analysis..... 977
Sodium carbonate, precipitation of calcium and magnesium by..... 732
Sodium palmitate, stearate, etc..... 526
Sodium zinc cyanide..... 570
Soils, Cuban, 5; Determination of potash, 491; Determination of total alkalies, 496; Determination of total phosphoric acid, 491; Hawaiian, fixation of ammonia and potash by, 47; Influence of moisture on composition of plant parts..... 1234
Solubilities of lead halides..... 469
Solutions, action of metallic magnesium on aqueous, 380; Freezing-points of dilute, 291; Study of..... 186
Sorghum, prussic acid in..... 55
Specific gravity of urine, relation to solids present..... 257
Specific rotation of some vegetable proteins..... 842
Starch, hydrolysis of, by acids, 1003; Maltose in products of hydrolyzed..... 1015
Steel, color test in high-carbon, 999; Determination of molybdenum in, 215; Rapid determination of phosphorus in, 772; See also Iron and steel.
STEHMAN, JOHN V. R. A platinum crucible for carbon combustions..... 237
STIEGLITZ, JULIUS. The theories of indicators..... 1112
Still, an improved testing..... 814
STILLMAN, J. M., and A. J. Cox. On certain factors influencing the precipitation of calcium and magnesium by sodium carbonate..... 732
Strontium: bismuthico-tungstate..... 1233
Succinyl chloride, action of aniline on..... 621
Sugar: coloring-matter in, 857; Reducing, disappearance in sugar-cane..... 855
Sugar analysis, International Commission for uniform methods..... 1208

Sugar-beet, relation of soil moisture to composition..... 1240
Sugar-cane, disappearance of reducing sugar in..... 855
p-Sulphocinnamic acid, derivatives of..... 622
Sulphur, determination in coal and coke.....184, 1265
Sulphuric acid, action of fuming, on isoamyl chloride..... 932
SUNDSTROM, CARL. A rapid method for determining sulphur in coal and coke.... 184
SY, ALBERT P. A new stability test for nitrocellulose powders..... 549
Syrup, determination of glucose in..... 982

TABLE for calculation of chemical weights..... 537
TAGGART, WALTER T. The electrolytic precipitation of nickel from phosphate solutions 1039
TAYLOR, FRANCIS O. Note on Perkin's test for bicarbonates..... 537
Tellurium, atomic weight, 226; Double halides with alkaloids..... 730
Tetrahedrite, analysis of..... 208
Thermochemical results, calculation of..... 209
Thiocyanates, normal heptyl..... 289
Thomas test, for explosives..... 553
THOMPSON, GUSTAVE W. Composition of the "break" from linseed oil..... 716
Thorium, and phenylhydrazine, 428; Behavior toward organic bases, 1128; Separation from beryllium..... 433
Tin, effect of carbon in iron on test for, 876; Rapid electrolytic precipitation.... 904
Titanium, separations of.....425, 430, 1076 ff
Titrations with potassium iodate..... 756
TITUS, WINIFRED. See V. Lenher.
TOCH, MAXIMILIAN. The permanent protection of iron and steel..... 761
TOLMAN, L. M. See L. S. Munson.
TOLMAN, L. M., and L. S. Munson. Iodine absorption of oils and fats..... 244
TRAPHAGEN, F. W., and Edmund Burke. Occurrence of salicylic acid in fruits... 242
Triphenylmethyl, existence of bodies analogous to..... 1274
Triphenylmethyl acetate..... 1269
Tryptophane reaction..... 853
TUFTS, CHARLES G. See Augustus H. Gill.
Tungsten, new complex acids of..... 298

UNDISSOCIATED salt, lecture experiment..... 996
Uranium, atomic weight, 229; Separation of bismuth from..... 97
Ureas, normal, a class of pseudothioureas described as..... 719
Ureine 1280
Uric acid, influence of diet, etc., on formation in man..... 1159
Urine, relation of specific gravity to solids present.....257, 871

VANADIUM, new complex acids of..... 298
VAN SLYKE, L. L., H. A. Harding and E. B. Hart. Rennet enzyme as a cause of chemical changes in the proteids of milk and cheese..... 1243
VEITCH, F. P. On the colorimetric determination of phosphoric acid, etc..... 169
Vicilin 339
Vieille test, for explosives..... 554
Vinegar, effect of fermentation on composition..... 16
Viscosity, modification of Babcock-Blasdale test, 968; Of soap solution as a factor in oil analysis..... 977

WALBRIDGE, W. K. See article by Treat B. Johnson..... 485
Walker method for determination of carbon dioxide..... 150
WALTERS, HARRY E. The volumetric determination of manganese in iron and steel..... 392
WALTERS HARRY E., and O. I. Affelder. The analysis of bronzes and bearing metals..... 632
Water, analysis from Hinton, W. Va..... 647

Water analysis, determination of carbonic acid, 742; Determination of phosphoric acid and silica..... 169
Water-blast, a cheap and efficient..... 770
Wheat kernels..... 1238
WHEELER, ALVIN S. Note on the bromination of heptane..... 532
WHEELER, HENRY L., and G. S. Jamieson. On a class of pseudothioureas described as normal ureas, 719; On some aldehyde condensation products, etc... 366
WHEELER, HENRY L., T. B. Johnson and D. F. McFarland. On the molecular rearrangement of unsymmetrical acylamidines into isomeric symmetrical derivatives..... 787
WHITNEY, W. R. The corrosion of iron..... 394
WHITNEY, W. R., and A. C. Melcher. An investigation of ammonia-silver compounds, etc..... 69
WIDTSOE, JOHN A. The influence of soil moisture upon the chemical composition of certain plant parts..... 1234
WIECHMANN, F. G. Fourth session of the International Commission for uniform methods of sugar analysis..... 1208
WILEY, H. W. Disappearance of reducing sugar in sugar-cane..... 855
Will test, for explosives..... 555
WILLIAMS, C. B. Methods for the determination of total phosphoric acid, etc., 491; See J. M. Pickel.
Wood, method of testing fire-proofed..... 406
WOODMAN, A. G. The determination of atmospheric carbon dioxide, etc..... 150
WORSTALL, R. A. Some chemical constants of fossil resins, 860; The action of fuming sulphuric acid upon isoamyl chloride..... 932

XANTHINE derivatives and fatigue..... 33

YTTERBIUM, atomic weight..... 229

ZEIN..... 847
Zinc, double cyanides with potassium and with sodium, 570; Rapid electrolytic precipitation, 899; Reduction of molybdenum by, 919; Separation of bismuth from, 93; Separation of copper from, 907; Separation of manganese from..... 1055
Zinc cyanide, action of alkalies on..... 587-592
Zinc oxide, action of alkali cyanides on..... 584, 586
Zirconium, behavior toward organic bases, 1128; Separation from beryllium, 432; Separation from iron..... 426

Additions to the Index for 1903.

(By mistake the following titles were omitted from the Index for the Journal for 1903.)

ABBOTT, A. C., and N. Gildersleeve. A study of the proteolytic enzymes and of the so-called hemolysins of some of the common saprophytic bacteria.....R 469
Adams, Frank D. The Monteregian Hills—a Canadian petrographical province...R 348
Adams, George I. Zinc and lead deposits of Northern Arkansas.....R 347
Allan, F. B., and J. S. DeLury. A new double oxalate of bismuth and potassium.... 728
Allan, F. B., and T. A. Phillips. A new double oxalate of bismuth and ammonium.. 729
Allen, S. J. See E. Rutherford.
Alwood, W. B. A study of cider-making in France, Germany, and England, etc. .R 334
Archbold, George. Cassava as a competitor of maize in the production of starch and allied products.....R 326
Auchy, George. The color test in high carbon steels..... 999
Avery, S. Note on the Avery-Beans method for the determination of arsenious acid in Paris green..... 1096

BANCROFT, W. D. Constant voltage and constant current separations .....R 382
Bartow, Edward, and Elmer V. McCollum. Some Kansas petroleum.....R 477
Benedict, Stanley and J. F. Snell. A method for the detection of chlorides, bromides and iodides 809
Bogert, Marston T., and L. Boroschek. Note on the mononitro-*o*-phthalic acids..... 767
Boroschek, L. See Marston T. Bogert.
Brooks, R. O. Report on the examination of foods, drugs, and public water supplies.....R 483
Brown, Orville H. The immunity of Fundulus eggs and embryos to electrical stimulation .....R 323

CAMPBELL, H. D., and J. L. Howe. A new (?) meteoric iron from Augusta County, Virginia.....R 349
Carnegie, Andrew. Organization and management.....R 450
Chase, Richard F. The influence of certain alcoholic liquors and tea and coffee, upon digestion in the stomach .....R 369
Clarke, F. W. A pseudo-serpentine from Stevens County, Washington.....R 298
Clowes, G. H. A. The relationship between the freezing-point depression and specific gravity of wine, etc .....R 394
Cooper, J. B. Treatment of Lake copper.....R 388
Couturier, F. See L. Vignon.
Cox, Irving J. See William A. Noyes.
Croftan, Alfred C. Synopsis of experiments on the transformation of circulating uric acid in the organism of man and animals.....R 399

DAVIS, W. W. Blast-furnace conditions affecting the chemical composition of foundry iron.....R 452
DeLury, J. S. See F. B. Allan.
Diller, J. S. Description of Port Orford triangle, R 297; Klamath Mountain section, California.....R 301
Doolittle, C. H. The matting of ores at Leadville and Robinson, Colorado.....R 388

EASTON, WM. H. The reduction of nitric acid in metallic nitrates to ammonia by the electric current..... 1042
Exner, Franz F. The rapid precipitation of metals in the electrolytic way..... 896

FALK. M. J. See H. C. Sherman.
Farrington, E. H. The composition of frozen milk.....R 411

Ferrell, Joseph L. Apparatus for, and methods of, treating wood to protect it from fire and preserve it from decay.....R 475
Field, H. E. Specifications for foundry pig iron.....R 453

GARNER, W. W. See A. M. Garner; See A. Michael.
Gildersleeve, N. See A. C. Abbot.
Goss, A. Ash analyses of some New Mexico plants .....R 409
Grant, Ulysses S. Preliminary report on the lead and zinc deposits of Southwestern Wisconsin.....R 349

HALL, J. L. Effect of superheated steam upon the tensile strength of alloys.....R 389
Hayes, C. W., and William Kennedy. Oil fields of the Texas-Louisiana Gulf coastal plain .....R 442
Henry, Carl D. The white country granite of West Sugarloaf or Bald Mountain, Boulder County, Colorado.....R 437
Hoffman, G. Chr. Report of the section of chemistry and mineralogy.....R 441
Howe, James L. See H. D. Campbell.
Hummel, J. A. See H. Snyder.
Hutton, R. S. Acetylene dissolved in acetone... .....R 401

JACKSON, FLORENCE. The delicacy of tests employed for the detection of metals, 992
Johnson, J. E. Some unusual crystals of cast iron.....R 385
Johnson, W. McA. Notes on physical characteristics of electrodeposited metals...R 360

KASTLE, J. H., and A. S. Loevenhart. The catalytic decomposition of hydrogen peroxide .....R 433
Kennedy, William. See C. W. Hayes.
Kirkbride, J. E. The Boulder oil field, Colorado.....R 330
Knight, S. S. The iron industry of the Birmingham district.....R 451

LADD, E. F. Report of the chemist .....R 484
Lakes, A. The present oil situation in Colorado.....R 383
Landes, Henry, and C. A. Ruddy. Coal deposits of Washington.....R 442
Lindgren, Waldemar. The geological features of the gold production of North America.....R 345
Loevenhart, A. S. See J. H. Kastle.

MACALLUM, A. B. On the inorganic composition of the Medusae. *Aurelia flavidula and Cyanea arctica*..... R 323
McCollum, Elmer V. See Edward Bartow.
McGillivray, J. D. Methods and values on the Yukon..... R 461
McLennan, J. C. Induced radioactivity excited in air at the foot of waterfalls.....R 431
Meltzer, Clara. See S. J. Meltzer.
Meltzer, S. J., and Clara Meltzer. On the effects of subcutaneous injection of the extract of the suprarenal capsule upon the blood vessels of the rabbit's ear...R 395
Mendel, Lafayette B (for H. C. Thacher). On secretin and lymph flow.....R 399
Merriam, E. S. See R. B. Riggs.
Michael, Arthur, and W. W. Garner. Further consideration of isocinnamic acid..R 363
Moldenke, R. Malleable cast iron..... ....R 456

NOYES, A. A., and G. V. Sammet. Experimental study of the thermodynamic relation between the heat of solution and the change of solubility with the temperature in the case of dissociated substances.....R 423
Noyes, William A., and Irving J. Cox. Synthesis of β-methyladipic acid 1093

OUTERBRIDGE, A. E., JR. Strength of white iron castings as influenced by heat treatment.....R 455

PATERSON, C. S. See J. W. Walker.
Patterson, S. B. The quality of pig iron for foundry use as shown by fracture and analysis.....R 452
Peters, E. D. Treatment of low-grade copper ores.....R 459

Phelps, C. S. Pot experiments with nitrogenous fertilizers.....R 407
Phillips, T. A. See F. B. Allan.
Postlethwaite, R. H. Present practice in gold dredging.....R 391
Preston, H. L. The Reed City meteorite.....R 298

RAMSEY, ROLLA R. The change of volume in Clark and cadmium cells and its relation to change of electromotive force due to pressure.....R 422
Ransome, F. L. The copper deposits of Bisbee, Arizona.....R 353
Richardson, George B. The upper red beds of the Black Hills.....R 439
Ries, Heinrich. Lime and cement industries of New York.....R 350
Riggs, R. B. The preparation of oxygen..... 876
Riggs, R. B., and E. S. Merriam. Note on the effect of combined carbon in iron on the test for tin..... 876
Ruddy, C. A. See Henry Landes.
Rutherford, E. Excited radioactivity and the method of its transmission, R 430; The magnetic and electric deviation of the easily absorbed rays from radium, R 431
Rutherford, E., and S. J. Allen. Excited radioactivity and ionization of the atmosphere.....R 429

SAHLIN, A. American conditions and competition.....R 450
Sammet, G. V. See A. A. Noyes.
Shedd, S. Building and ornamental stones of Washington.....R 442
Sherman, H. C., and M. J. Falk. The influence of atmospheric oxidation upon the analytical constants of fatty oils..... 711
Shimer, Porter W. Note on carbon combustion in a platinum crucible..... 997
Shiver, F. S. A rotation study.....R 408
Silver, L. P. Petrography of some igneous rocks of the Kettle River Mining Division, British Columbia.....R 441
Smith, Bernard H. A comparative study of methods of determining formaldehyde..... 1028
Smith, Edgar F. Metal separations in the electrolytic way..... 892
Snyder, H., and J. A. Hummel. Alfalfa: its chemical development, feeding value, and digestibility.....R 331
Sollman, Torald. The effect of saline injections, etc., on the chloride constant of the urine of the dog.....R 396, 469
Stewart, G. N. Differences of potential between blood and serum, and between normal and laked blood.....R 397

THACHER, HENRY C. See Lafayette B. Mendel.
Tolman, L. M., and L. S. Munson. Olive oils and olive oil substitutes..... 954
Trowbridge, John. Gaseous constitution of the H and K lines of the solar spectrum, etc.....R 425

VAN ARSDALE, G. D. A proposed process for extracting copper from low-grade ores.....R 460
Vignon, L., and F. Couturier. The rôle of nitrate and phosphate fertilizers in the richness of wheat in gluten.....R 481
Voorhees, E. B. Field experiments with nitrate of soda on forage crops and on market garden crops, R 480; Investigations relative to the use of nitrogenous materials.....R 480

WALKER, A. W. A device for ascertaining average silicon in a foundry iron mixture.....R 452
Walker, J. W., and C. S. Paterson. Influence of impurities in salt upon the yield of caustic soda by the amalgam process.....R 405
Warman, P. C. Catalogue and index of the publications of the U. S. Geological Survey, 1901 to 1908.....R 442
Washington, Henry S. Chemical analyses of igneous rocks published from 1884 to 1900, etc.....R 442
Waters, C. E. The action of ozone on carbon monoxide.....R 435
Watson, Thomas L. A preliminary report on a part of the granites and gneisses of Georgia.....R 302

Watts, A. S. The composition of porcelains for electrical purposes..... ..R 330
Weed, Walter H. Copper deposits of New Jersey..... ..... R 442
Wheeler, Henry L., and T. B. Johnson. Synthesis of aminooxypyrimidines having the composition of cytosine..... .....R 319
Wilder, F. A. The fuel value of North Dakota lignites .....R 329
Wiley, H. W. Crystals of oxalate of lime in plants.....R 481
Winton, A. L., *et al.* Seventh report on food products.....R 482
Withers, W. A., and G. S. Fraps. The sulphur content of some vegetable material ....R 409